LIGAND VARIATION IN MOLYBDENUM ASYMMETRIC RING-CLOSING METATHESIS CATALYSTS

by

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B.Sc. (Honours) in Chemistry, University of British Columbia
(1997)

Submitted to the Department of Chemistry
in Partial Fulfillment of the Requirements
for the Degree of

DOCTOR OF PHILOSOPHY
at the
MASSACHUSETTS INSTITUTE OF TECHNOLOGY
June 2002

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Dedicated to everyone who cheered me on towards the finish line,
especially Mom, Dad, Joe, Oma and Brad.

It is only in the still pond that the stars are reflected.

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ABSTRACT

Chapter 1

Complexes containing halogenated arylimido ligands were synthesized and characterized. $Mo(NAr)_2Cl_2(dme)$ complexes were synthesized where NAr = N-2-IC_6H_4 (**1**), N-2,4,6-$F_3C_6H_2$ (**3**), N-2,4,6-$Cl_3C_6H_2$ (**4**), N-2,6-Br_2-4-$CH_3C_6H_2$ (**7**), and N-2,6-$Cl_2C_6H_3$ (**11**). $Mo(NAr)_2(CH_2CMe_3)_2$ complexes were synthesized where NAr = N-2-I-C_6H_4 (**2**), N-2,4,6-$Cl_3C_6H_2$ (**6**), N-2,6-Br_2-4-$CH_3C_6H_2$ (**8**), and N-2,6-$Cl_2C_6H_3$ (**12**). $Mo(NAr)_2(CH_2CMe_2Ph)_2$ complexes were synthesized where NAr = N-2,4,6-$Cl_3C_6H_2$ (**5**), and N-2,6-$Cl_2C_6H_3$ (**13**). Bistriflate complexes Mo(N-2,6-Br_2-4-$CH_3C_6H_2$)$(CHCMe_3)(OTf)_2(dme)$ (**9**), Mo(N-2,6-$Cl_2C_6H_3$)$(CHCMe_3)(OTf)_2(dme)$ (**14**), and Mo(N-2,6-$Cl_2C_6H_3$)$(CHCMe_2Ph)(OTf)_2(THF)_x$ (**15**) were isolated. Using these bistriflate complexes, Mo(N-2,6-Br_2-4-$CH_3C_6H_2$)$(CHCMe_3)$(*R*-benzhydril)(THF) (**10**), Mo(N-2,6-$Cl_2C_6H_3$)$(CHCMe_3)$(*S*-biphen)(THF) (**16**), Mo(N-2,6-$Cl_2C_6H_3$)$(CHCMe_3)$(±-biphen)(THF) (**16rac**), Mo(N-2,6-$Cl_2C_6H_3$)$(CHCMe_3)$(*R*-benzhydril)(THF) (**17**), Mo(N-2,6-$Cl_2C_6H_3$)$(CHCMe_3)$(*S*-biad) (**18**), Mo(N-2,6-$Cl_2C_6H_3$)$(CHCMe_3)$(*R*-TRIP)(THF) (**19**), and Mo(N-2,6-$Cl_2C_6H_3$)$(CHCMe_3)$(*R*-mesbitet)(THF) (**20**) were synthesized. The X-ray crystal structures of **16** and **17** were determined. Complexes **10**, **16-20** catalyzed the ring-closing metathesis of olefins, with complexes **10**, **16**, **17**, **19** and **20** showing high enantioselectivities in two desymmetrization reactions. Complex **16rac** reacts with ethylene to give the first stable olefin decomposition complex, Mo(N-2,6-$Cl_2C_6H_3$)(±-biphen)(η^2-C_2H_4) (**29**).

Chapter 2

The diamine 2,2'-bis-*p*-tolylsulfonamido-1,1'-binaphthyl (**30**; $[BINA(NTs)_2]H_2$) was synthesized by reaction of 2,2'-diamino-1,1'-binaphthyl with pyridine and *p*-toluenesulfonyl chloride. Deprotonation of **30** with benzyl potassium followed by addition to Mo(N-2,6-i-

$Pr_2C_6H_3$)(CHCMe$_2$Ph)(OTf)$_2$(dme) (OTf = OSO_2CF_3), Mo(N-2-$CF_3C_6H_4$)(CHCMe$_2$Ph)(OTf)$_2$(dme) and Mo(N-2-$CF_3C_6H_4$)(CHCMe$_3$)(OTf)$_2$(dme) gave Mo(N-2,6-i-$Pr_2C_6H_3$)(CHCMe$_2$Ph)[BINA(NTs)$_2$] (**31**), Mo(N-2-$CF_3C_6H_4$)(CHCMe$_2$Ph)[BINA(NTs)$_2$] (**32**) and Mo(N-2-$CF_3C_6H_4$)(CHCMe$_3$)[BINA(NTs)$_2$] (**33**), respectively. The X-ray crystal structure of **33** showed that one sulfonyl oxygen is coordinated to molybdenum. The diamines 2,2'-bis(trimethylsilyl)amido-1,1'-binaphthyl (**34**; [BINA(NTMS)$_2$]H$_2$) and 2,2'-bis(isopropyl)amido-1,1'-binaphthyl (**36**; [BINA(N-i-Pr)$_2$]H$_2$) were deprotonated with methyllithium and then each reacted with Mo(N-2,6-i-$Pr_2C_6H_3$)(CHCMe$_2$Ph)(OTf)$_2$(dme) to give Mo(N-2,6-i-$Pr_2C_6H_3$)(CHCMe$_2$Ph)[BINA(NTMS)$_2$] (**35**) and Mo(N-2,6-i-$Pr_2C_6H_3$)(CHCMe$_2$Ph)[BINA(N-i-Pr)$_2$] (**37**), respectively. The X-ray crystal structure of **37** was obtained, confirming its pseudotetrahedral nature. None of these complexes reacts readily with ethylene, styrene, benzaldehyde, or diallyl ether.

Chapter 3

In one reaction of [±-biphen]K$_2$ with Mo(N-2,6-$Cl_2C_6H_3$)(CHCMe$_3$)(OTf)$_2$(dme), the amido alkylidyne product, Mo(NH-2,6-$Cl_2C_6H_3$)(CCMe$_3$)(±-biphen) (**41**) was isolated. In another separate reaction, [*S*-biphen]K$_2$ reacted with Mo(N-2,6-$Cl_2C_6H_3$)(CHCMe$_2$Ph)(OTf)$_2$(THF)$_x$ to give the amido alkylidyne product Mo(NH-2,6-$Cl_2C_6H_3$)(CCMe$_2$Ph)(*S*-biphen) (**42**). Complex **42** was characterized by X-ray crystallography. Attempts to isolate **41** and **42** in other reactions were not successful. Heating a solution of Mo(η^2-$H_2CCSiMe_3$)[N(i-Pr)Ar"]$_3$ (Ar" = 3,5-$Me_2C_6H_3$) to 80 °C in toluene generated Mo(CCH_2SiMe_3)[N(i-Pr)Ar"]$_3$ which then reacted with one equiv [±-biphen]H$_2$ to give the molybdenum amido alkylidyne bisaryloxide complex, Mo(CCH_2SiMe_3)[N(i-Pr)Ar"](±-biphen) (**43**). This complex was identified by ^{1}H NMR (500 MHz, toluene-d_8) however it was not isolated. Addition of one equiv 1-adamantanol to **43** gave Mo(CCH_2SiMe_3)(±-biphen)(OAd) (**44**) as a white crystalline solid. The X-ray crystal structure of **44** was determined. Complex **44** reacted with 2-butyne and 3-hexyne to give the metallacyclobutadiene complexes Mo(C_3Me_3)(±-biphen)(OAd) (**45**) and Mo(C_3Et_3)(±-biphen)(OAd) (**46**), respectively. Complexes **45** and **46** were not effective alkyne metathesis catalysts. Both complexes were stable in the solid state over several days, but slowly decomposed in solution. The structure of the product of decomposition of **45** was determined by X-ray crystallography. The mechanism by which this decomposition product, Mo(decomp-biphen)(η^2-C_2Me_2)(OAd) (**47**), was obtained is unknown.

Appendix A

The diamine 2,2'-bis-*p*-tolylsulfonamido-1,1'-binaphthyl (**30**; [BINA(NTs)$_2$]H$_2$) reacted with Zr(CH_2Ph)$_4$ and Zr(NMe_2)$_4$ to give [BINA(NTs)$_2$]Zr(CH_2Ph)$_2$ (**A-3**) and

$[BINA(NTs)_2]Zr(NMe_2)_2$ (**A-5**), respectively. Complex **A-3** was activated with $[Ph_3C][B(C_6F_5)_4]$ to give $\{[BINA(NTs)_2]Zr(CH_2Ph)\}[B(C_6F_5)_4]$ (**A-4**) which was detected by ^1H NMR (500 MHz, C_6D_5Br) and which appeared to oligomerize 1-hexene at 60 °C.

Appendix B

Treatment of 2-bromophenol, 2-bromobenzyl alcohol and 2-bromo-6-t-butyl-4-methylphenol with 2 equiv butyllithium followed by 1 equiv *R*-fenchone yielded 2-fencholphenol (**B-1**), 2-fencholbenzyl alcohol (**B-2**) and 2-t-butyl-6-fenchol-4-methylphenol (**B-3**). Complexes of these diols of the type $Mo(N\text{-}2,6\text{-}i\text{-}Pr_2C_6H_3)(CHCMe_2Ph)(OR)_2$ were not isolated.

Thesis Supervisor: Dr. Richard R. Schrock
Title: Frederick G. Keyes Professor of Chemistry

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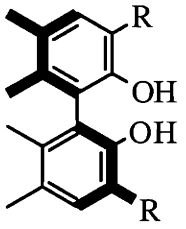
List of Schemes

List of Abbreviations

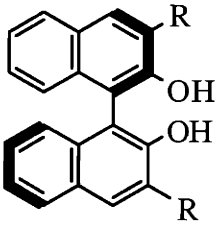
Ac	acetate, $C(O)CH_3$
Ad	1-adamantyl
ADMET	acyclic diene metathesis
Anal. Calcd.	Elemental Analysis Calculated
anti	alkylidene rotamer with hydrogen directed towards imido
Ar	aryl
Ar"	3,5-dimethylphenyl, 3,5-$Me_2C_6H_3$
ARCM	asymmetric ring-closing metathesis
Å	Angstroms
[BINA(N-i-Pr)$_2$]H$_2$	N,N'-bis(*iso*-propyl)-2,2'-diamino-1,1'-binaphthyl
[BINA(NTMS)$_2$]H$_2$	N,N'-bis(trimethylsilyl)-2,2'-diamino-1,1'-binaphthyl
[BINA(NTs)$_2$]H$_2$	2,2'-bis-*p*-tolylsulfonamido-1,1'-binaphthyl
br	broad
Calcd.	calculated
config	configuration
conv	conversion
Cy	cyclohexyl
d	doublet
dme	1,2-dimethoxyethane
ee	enantiomeric excess
equiv	equivalent
eq	equation
Et	ethyl, CH_2CH_3
ether	diethyl ether
Fc	ferrocenyl
g	grams
GLC	gas-liquid chromatography
h	hour(s)
HRMS	high resolution mass spectroscopy
Hz	Hertz
i-Pr	*iso*-propyl, $CH(CH_3)_2$
J	coupling constant in Hertz
K	degrees Kelvin
L	liter

m	multiplet
M	moles per liter, mol/L
Me	methyl, CH_3
Mes	mesityl, 2,4,6-trimethylphenyl, 2,4,6-$Me_3C_6H_2$
mg	milligram
MHz	megahertz
min	minutes
mL	milliliter
mmol	millimole
mol	mole
NMR	nuclear magnetic resonance
ORTEP	Oak Ridge Thermal Ellipsoid Plot
OTf	OSO_2CF_3, triflate, trifluoromethanesulfonate
pent	pentyl, $(CH_2)_4CH_3$
Ph	phenyl, C_6H_5
ppm	parts per million
Pr	propyl, $CH_2CH_2CH_3$
psi	pressure in pounds per square inch
py	pyridine
RCM	ring-closing metathesis
ROMP	ring-opening metathesis polymerization
s	singlet
sept	septet
syn	alkylidene rotamer with hydrogen directed away from imido
t	triplet
t-Bu	*tert*-butyl, $C(CH_3)_3$
Temp	temperature
THF	tetrahydrofuran
TMS	trimethylsilyl, $SiMe_3$
TRIP	2,4,6-tri-*iso*-propylphenyl, 2,4,6-i-$Pr_3C_6H_2$
Ts	tosylate, *para*-tolylsulfonate, 4-$MeC_6H_4SO_2$
°C	degrees Celcius
±	racemic

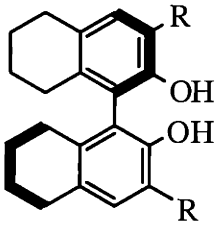
List of Diols for Reference



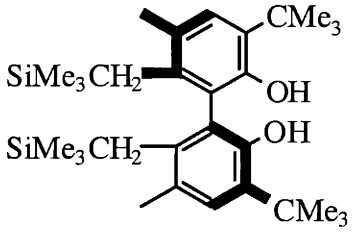
[*S*-biphen]H_2 (R = CMe_3)
[*S*-biad]H_2 (R =1-adamantyl)



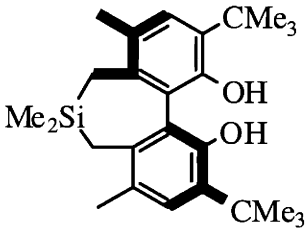
[*R*-TRIP]H_2 (R = 2,4,6-i-$Pr_3C_6H_2$)
[*R*-mesitylbinap]H_2 (R = 2,4,6-$Me_3C_6H_2$)



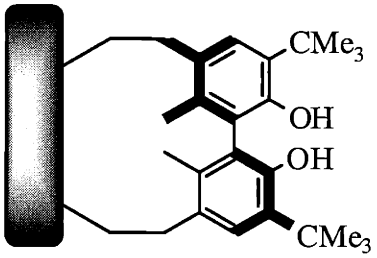
[*R*-bitet]H_2 (R = CMe_3)
[*R*-mesbitet]H_2 (R = 2,4,6-$Me_3C_6H_2$)
[*R*-benzhydril]H_2 (R = $CHPh_2$)



[*S*-TMS_2biphen]H_2



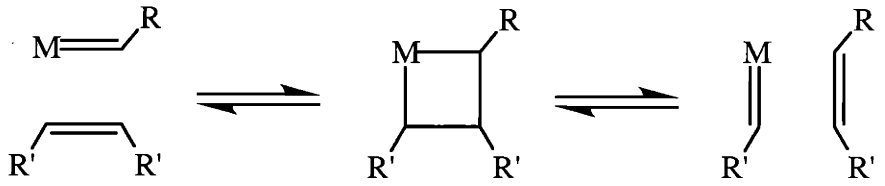
[*S*-biphen$SiMe_2$]H_2



polymer-supported [*S*-biphen]H_2

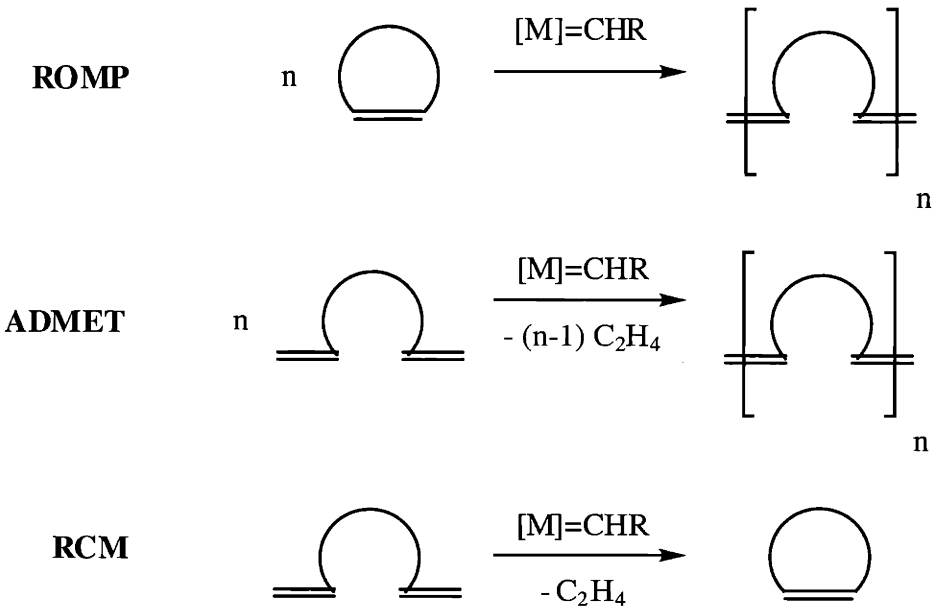
GENERAL INTRODUCTION

Catalytic olefin metathesis is a powerful tool for breaking and forming C=C double bonds.[1,2] The mechanism of this process involves the 2 + 2 addition of an olefin to a transition metal alkylidene complex to give an unstable metallacyclobutane intermediate. This intermediate then undergoes non-selective cycloreversion to generate a new metal alkylidene and olefin or regenerate the starting materials (Scheme I.1).



Scheme I.1. Mechanism of Olefin Metathesis.

Olefin metathesis has found practical application in many synthetic processes, including ring-opening metathesis polymerization (ROMP), acyclic diene metathesis (ADMET) and ring-closing metathesis (RCM) (Scheme I.2).[2-4] ROMP is a process in which a strained cyclic olefin, such as norbornene, is opened and then polymerized.[5-7] ADMET involves the intermolecular



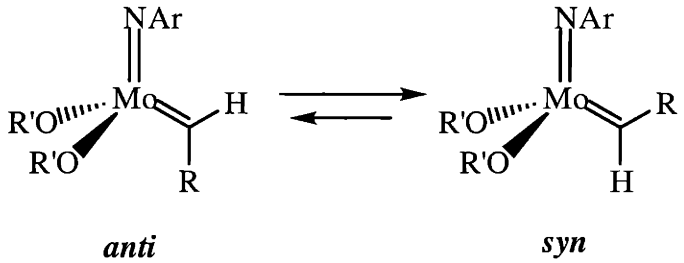
Scheme I.2. Olefin metathesis processes.

reaction of dienes to form oligomers or polymers.[8-12] RCM is the intramolecular reaction of a diene to form a cyclic olefin.[13-15] ADMET and RCM are driven to completion by the elimination of volatile olefin by-products such as ethylene or propylene, while ROMP is driven to completion by the relief of ring-strain in the cyclic olefin.

Many olefin metathesis catalysts have been studied and those based on molybdenum, tungsten and ruthenium have found the widest application. Molybdenum[16-18] and tungsten[18-20] imido alkylidene bisalkoxide complexes of the type $M(NAr)(CHR)(OR')_2$ are highly reactive olefin metathesis catalysts, while ruthenium alkylidene complexes,[21] $Ru(CHR)(PCy_3)_2Cl_2$, are less reactive. Ru has the advantage, however, of being reactive in the presence of water and oxygen, while Mo and W catalysts require strict anhydrous and air-free conditions.[22]

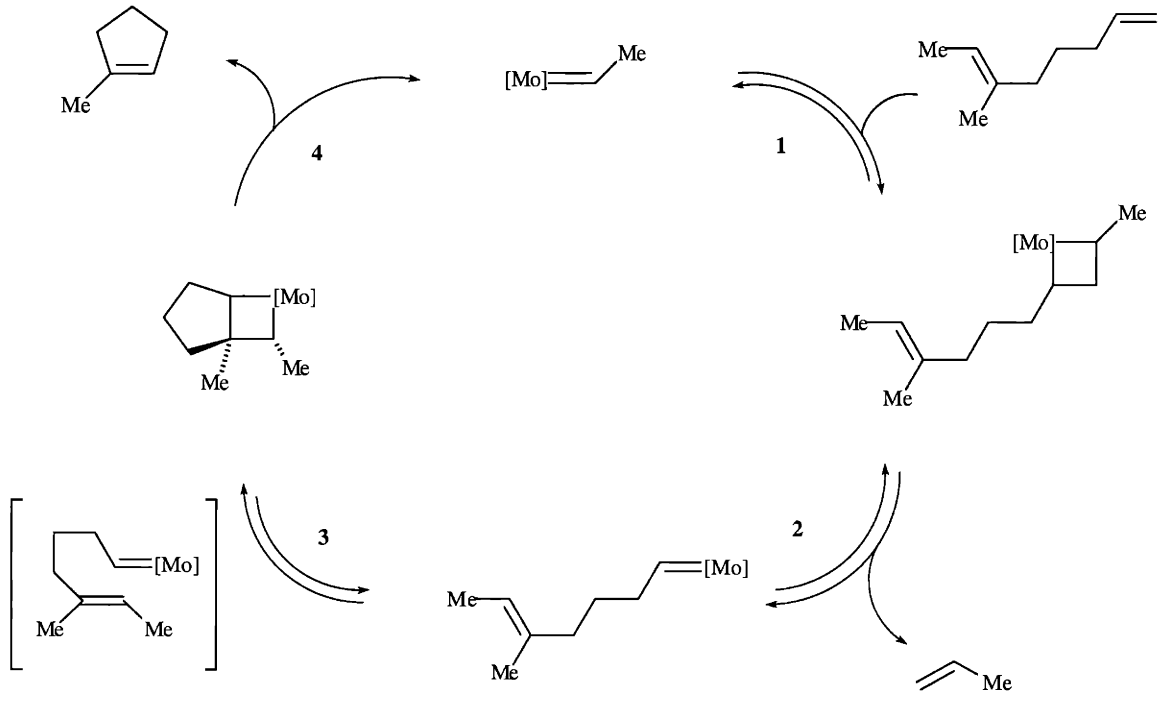
In focusing on the synthesis of catalysts for ring-closing metathesis, our group has mainly worked with molybdenum imido alkylidene bisalkoxide complexes. There are several reasons for focusing on Mo: the structure of these complexes is modular, meaning there are well-documented methods for the variation of the imido and bisalkoxide ligands;[16,23,24] and Mo complexes are more reactive because molybdacyclobutane intermediates break up more readily than W metallacyclobutane intermediates.[5]

Complexes of the type $Mo(NAr)(CHR)(OR')_2$ exist as a mixture of alkylidene isomers.[16,25] The alkylidene lies in the N_{imido}-Mo-$C_{alkylidene}$ plane either *syn*, with the alkylidene substituent directed towards the imido group, or *anti*, with the alkylidene substituent directed away from the imido group (Scheme I.3). The *syn* isomer is stabilized by an α-agostic interaction arising from donation of the C-H to molybdenum. Both *syn* and *anti* isomers occur in solution, however studies show that the *syn* isomer is the lowest energy species of the two.[25-28] The rate of exchange between *syn* and *anti* depends on the electrophilicity of the metal; complexes with more electron-withdrawing bisalkoxides such as $Mo(NAr)(CHR)[OCMe(CF_3)_2]_2$ have a slower rate of *syn/anti* exchange than $Mo(NAr)(CHR)(OCMe_3)_2$.[26] Mechanistic studies have also shown that the *anti* isomer is the more reactive of the two.[29]



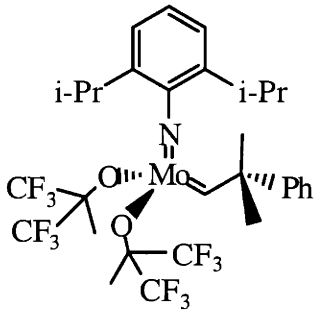
Scheme I.3. *Syn* and *anti* alkylidene isomers.

The mechanism of ring-closing metathesis is shown in Scheme I.4. The less sterically hindered olefin in a diene reacts with the molybdenum alkylidene complex to give a molybdacyclobutane intermediate (step 1) that is cleaved to eliminate propylene (step 2). The second olefin then undergoes an intramolecular metathesis reaction with the metal alkylidene (step 3) to give the ring-closed product and regenerate the catalyst (step 4).

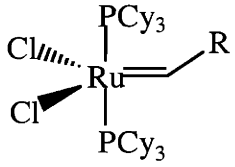


Scheme I.4. Mechanism of Ring-Closing Metathesis.

The most widely used achiral catalysts for ring-closing metathesis include Mo(N-2,6-i-$Pr_2C_6H_3$)(CHCMe$_2$Ph)[OCMe(CF$_3$)$_2$]$_2$ (**I-1**),[16,30-32] and Ru(CHR)(PCy$_3$)$_2$Cl$_2$ (R = Ph, CH=CPh$_2$) (**I-2**).[33,34] A major target has been the development of chiral complexes that

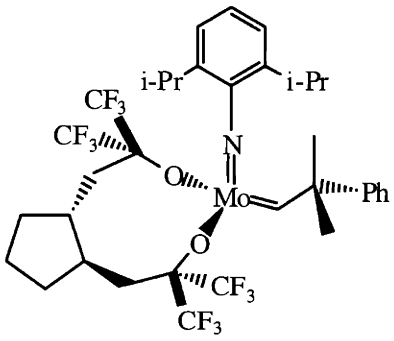


I-1

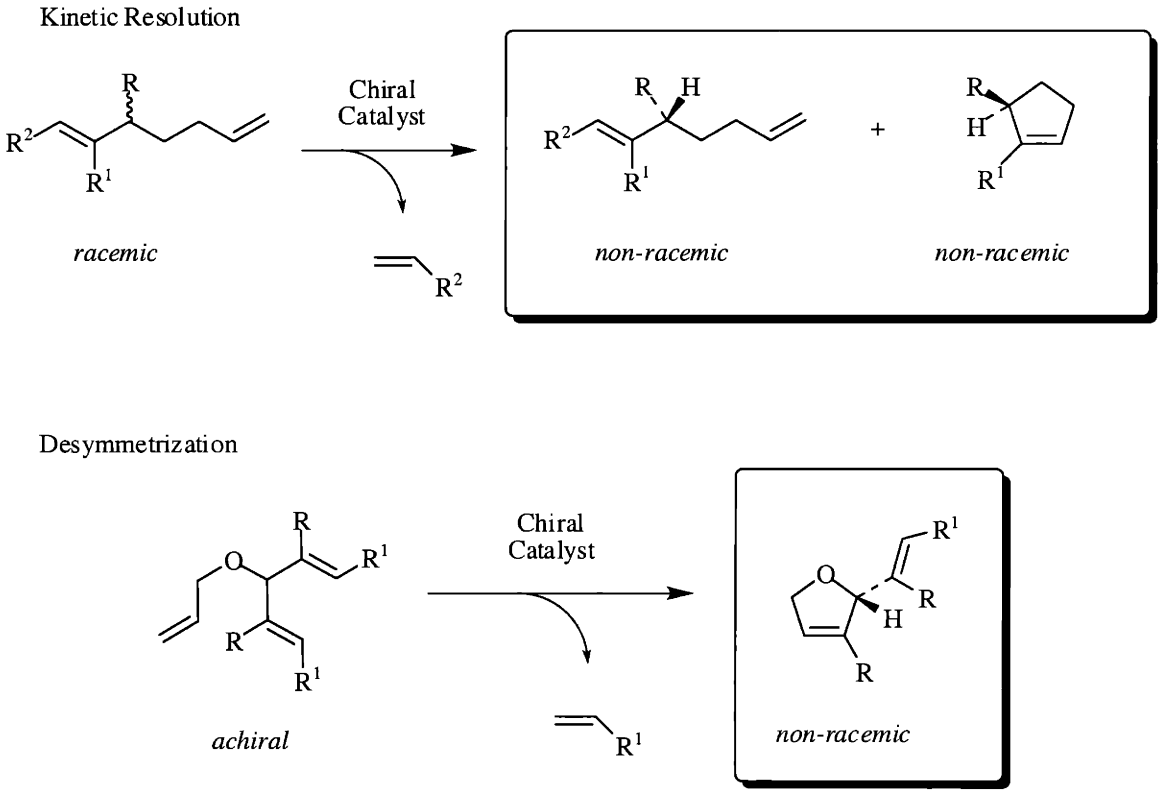


I-2

catalyze the asymmetric ring-closing metathesis (ARCM) of racemic substrates.[35] For example, a chiral metal alkylidene catalyst would react in the kinetic resolution of a racemic diene, selectively converting one enantiomer to ring-closed product and leaving the opposite enantiomer unreacted. In another example, a chiral metal alkylidene catalyst would react in the desymmetrization of an achiral triene, giving one enantiomer of ring-closed product (Scheme I.5). Early developments in the synthesis of catalysts for ARCM included the molybdenum imido alkylidene bisalkoxide complex **I - 3**. However, this

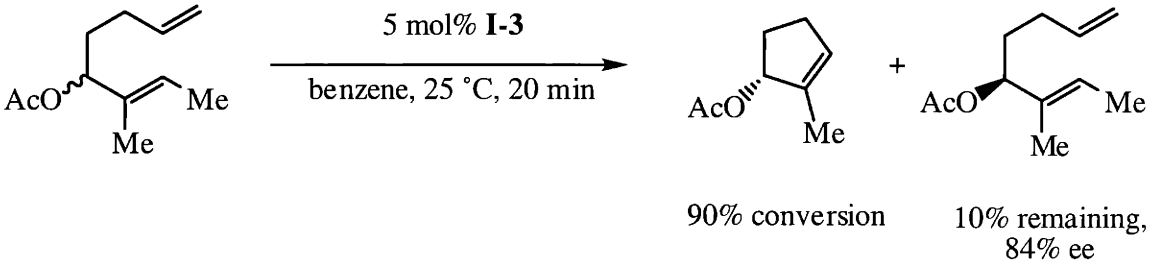


I-3



Scheme I.5. Asymmetric ring-closing metathesis processes: kinetic resolution and desymmetrization reactions.

catalyst showed poor efficiency in select kinetic resolution reactions (for example, eq 1).[36,37]

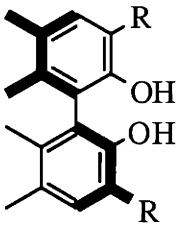


90% conversion 10% remaining, 84% ee (1)

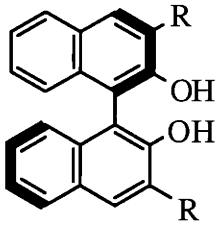
Previous results in our group had shown that molybdenum imido alkylidene complexes containing C_2-symmetric chiral binaphtholate or biphenolate-based ligands gave polymers with high tacticity by ROMP.[38,39] Inspired by these results, our group has recently prepared and studied a series of molybdenum imido alkylidene complexes containing optically pure C_2-symmetric bisaryloxide ligands derived from chiral diols including [*S*-biphen]H_2 (**I-4**),[40-42] [*R*-TRIP]H_2 (**I-5**),[43] [*S*-biad]H_2 (**I-6**),[42] [*R*-bitet]H_2 (**I-7**),[44] [*S*-TMS$_2$biphen]H_2 (**I-8**),[45] [*S*-biphenSiMe$_2$]H_2 (**I-9**),[45] [*R*-mesitylbinap]H_2 (**I-10**),[46] [*R*-mesbitet]H_2 (**I-11**),[47] [*R*-benzhydril]H_2 (**I-12**),[47] and the polymer-supported [*S*-biphen]H_2 (**I-13**).[48]

Molybdenum imido alkylidene complexes of **I-4** - **I-13** have shown remarkable reactivity and enantioselectivity in a wide range of asymmetric reactions performed by our collaborators in the Hoveyda group at Boston College. The reactions catalyzed by these complexes include: kinetic resolution of acyclic dienes containing silyl-protected alcohols (Figure 1**a**);[40] kinetic resolution of allylic ethers (Figure 1**b**);[41] enantioselective synthesis of dihydrofurans by desymmetrization (Figure 1**c**);[41] enantioselective heterocycle synthesis by kinetic resolution (Figure 1**d**) and desymmetrization (Figure 1**e**);[43,49] enantioselective synthesis of unsaturated pyrans from acyclic trienes (Figure 1**f**);[50] enantioselective spirocycle synthesis (Figure 1**g**);[51] desymmetrization of tetraenes to give cyclic ethers (Figure 1**h**);[52] desymmetrization of triene acetals (Figure 1**i**);[52] desymmetrization of dienes (Figure 1**j**) and trienes (Figure 1**k**) by tandem asymmetric ring-opening metathesis/ring-closing metathesis;[53] and tandem asymmetric ring-

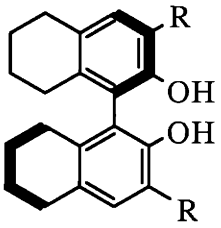
opening metathesis/cross metathesis of norbornene substrates (Figure 1l).[54,55] These results highlight the importance of ARCM as a synthetic tool.



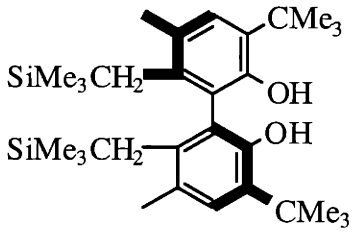
[*S*-biphen]H_2 (**I-4**, R = CMe_3)
[*S*-biad]H_2 (**I-6**, R = 1-adamantyl)



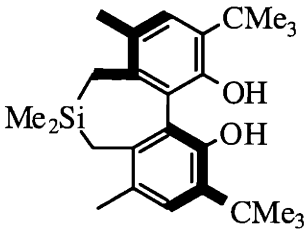
[*R*-TRIP]H_2 (**I-5**, R = 2,4,6-i-$Pr_3C_6H_2$)
[*R*-mesitylbinap]H_2 (**I-10**, R = 2,4,6-$Me_3C_6H_2$)



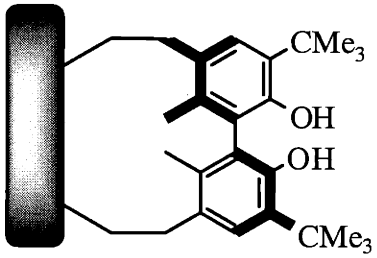
[*R*-bitet]H_2 (**I-7**, R = CMe_3)
[*R*-mesbitet]H_2 (**I-11**, R = 2,4,6-$Me_3C_6H_2$)
[*R*-benzhydril]H_2 (**I-12**, R = $CHPh_2$)



[*S*-TMS_2biphen]H_2 (**I-8**)



[*S*-biphenSiMe_2]H_2 (**I-9**)



polymer-supported [*S*-biphen]H_2 (**I-13**)

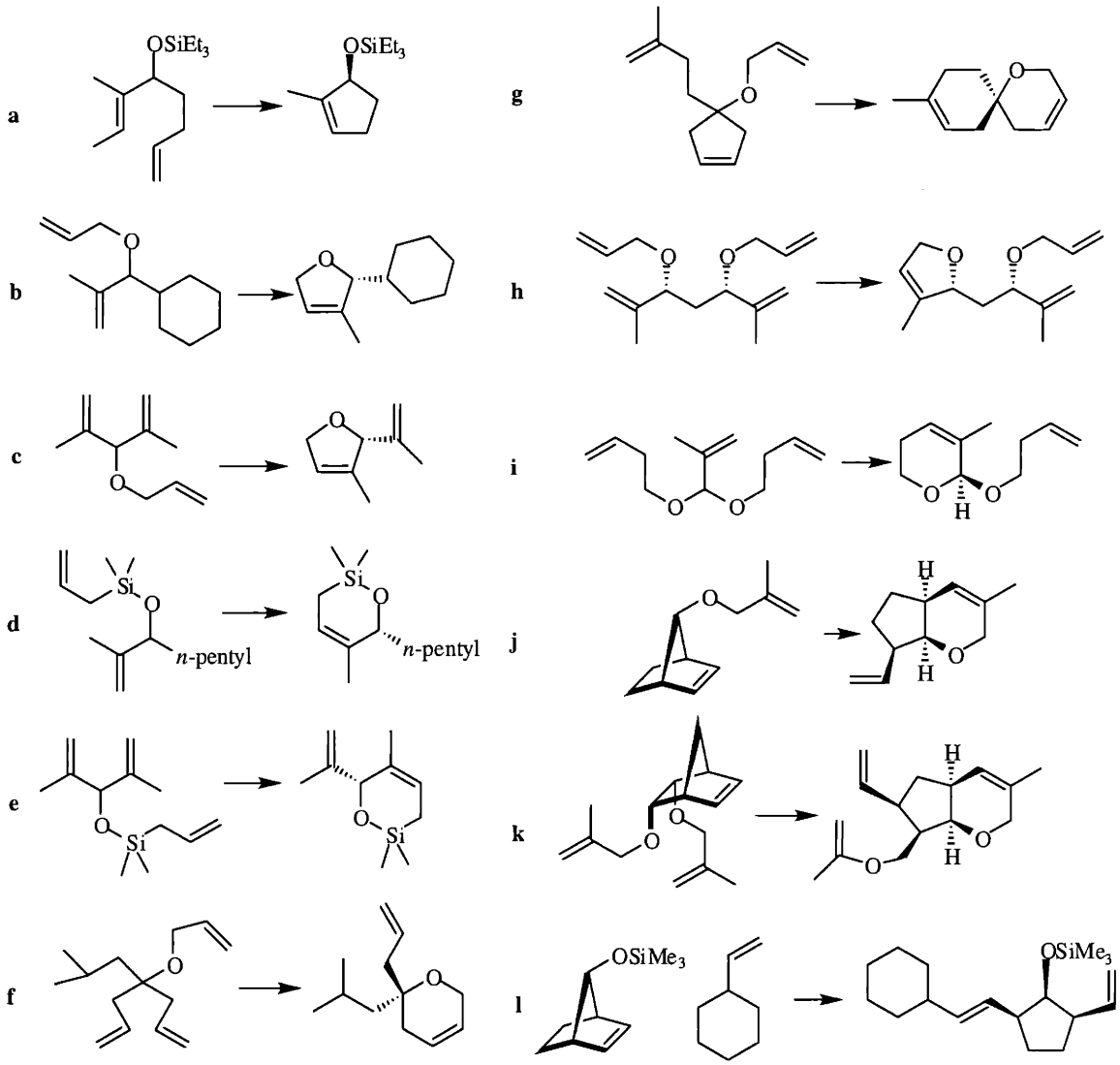


Figure I.1. Examples of catalytic asymmetric reactions.

While a major focus of research in our group is the variation of bisaryloxide ligands in ARCM catalysts, the work presented in this thesis will focus on different ligand variations in these Mo complexes. The synthesis and reactivity of complexes with halogenated arylimido groups, complexes with diamido groups in place of bisaryloxides, and attempts to synthesize alkylidenes via alkylidynes, are described.

Chapter 1

SYNTHESIS OF MOLYBDENUM COMPLEXES CONTAINING HALOGENATED IMIDO LIGANDS. NEW CATALYSTS FOR ASYMMETRIC RING-CLOSING METATHESIS CONTAINING 2,6-DICHLOROARYLIMIDO LIGANDS

A portion of this work has appeared in print:

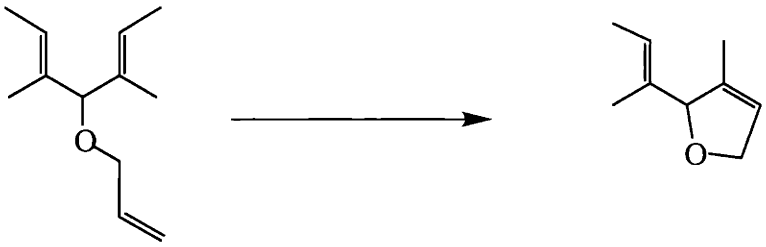
R.R. Schrock, J.Y. Jamieson, S.J. Dolman, S.A. Miller, P.J. Bonitatebus, Jr., A.H. Hoveyda. "New Chiral Molybdenum Catalysts for Asymmetric Olefin Metathesis that Contain 3,3'-Disubstituted Octahydrobinaphtholate or 2,6-Dichlorophenylimido Ligands" *Organometallics* **2002**, *21*, 409.

D.R. Cefalo, A.F. Kiely, M. Wuchrer, J.Y. Jamieson, R.R. Schrock, A.H. Hoveyda. "Enantioselective Synthesis of Unsaturated Cyclic Tertiary Ethers by Mo-Catalyzed Olefin Metathesis" *J. Am. Chem. Soc.* **2001**, *123*, 3139.

G.S. Weatherhead, J.H. Houser, J.G. Ford, J.Y. Jamieson, R.R. Schrock, A.H. Hoveyda. "Modular Mo-based Catalysts for Efficient Asymmetric Olefin Metathesis. Catalytic Enantioselective Synthesis of Cyclic Ethers and Acetals" *Tetrahedron Letters* **2000**, *41*, 9553.

INTRODUCTION

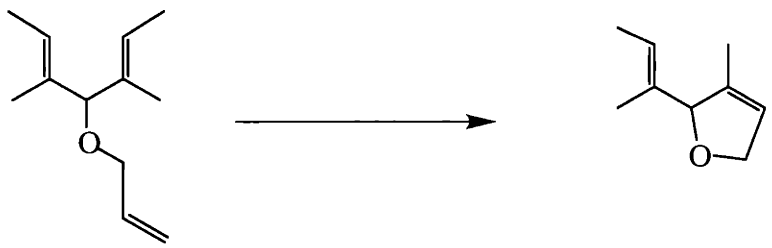
Early studies in our group showed that arylimido ligand variation in molybdenum imido alkylidene *S*-biphen and *S*-biad complexes affected the yield of ring-closed product, length of reaction time and product enantiomeric excesses in ARCM reactions.[40-42,56] For example, the desymmetrization of the triene (3,5-dimethyl-(2*E*,5*E*)-heptadienyl)allyl ether with 1 mol% Mo(N-2,6-i-$Pr_2C_6H_3$)($CHCMe_2Ph$)(*S*-biphen) leads to 32% conversion to ring-closed product (after 9h, with 94% ee) while Mo(N-2,6-$Me_2C_6H_3$)($CHCMe_2Ph$)(*S*-biphen) (1 mol%) leads to essentially complete conversion to ring-closed product (after 4h, with 99% ee) (Scheme 1.1).[41]



Mo(N-2,6-i-$Pr_2C_6H_3$)($CHCMe_2Ph$)(*S*-biphen)	32% conversion	94% ee
Mo(N-2,6-$Me_2C_6H_3$)($CHCMe_2Ph$)(*S*-biphen)	>95% conversion	99% ee

Scheme 1.1. Conversion to ring-closed product in desymmetrization reaction changes depending on imido group.

In the same desymmetrization reaction, Mo(N-2-$CF_3C_6H_4$)($CHCMe_3$)(*S*-biad) leads to complete conversion to ring-closed product within 1h (with 90% ee) while Mo(N-2,6-$Me_2C_6H_3$)($CHCMe_2Ph$)(*S*-biad) is much slower, requiring 18h (Scheme 1.2).[56] It is thought that the more electron-withdrawing imido group N-2-$CF_3C_6H_4$ makes the metal more electrophilic, such that it reacts faster with olefinic substrates.



Mo(N-2,6-$Me_2C_6H_3$)(CHCMe_2Ph)(*S*-biad)	18h	>95% conversion	86% ee
Mo(N-2-$CF_3C_6H_4$)(CHCMe_3)(*S*-biad)	1h	>95% conversion	90% ee

Scheme 1.2. Reaction times in desymmetrization changes depending on imido group.

The general synthetic route towards the precursors for ARCM catalysts is shown in Scheme 1.3.[16] In the first step, reaction of two equiv of an aniline ($ArNH_2$) with sodium molybdate in the presence of triethylamine, chlorotrimethylsilane and dimethoxyethane gives $Mo(NAr)_2Cl_2(dme)$. Reaction of this complex with two equiv of Grignard reagent, typically neopentylmagnesium chloride or 2-methyl-2-phenylpropylmagnesium chloride (neophylmagnesium chloride), gives the corresponding dialkylbis(imido)molybdenum complex, $Mo(NAr)_2(CH_2R)_2$. Addition of three equiv of triflic acid to the dialkyl complex results in the elimination of one imido group as anilinium triflate and α-abstraction to eliminate one alkyl group, giving $Mo(NAr)(CHR)(OTf)_2(dme)$.

$$Na_2MoO_4 \xrightarrow{a} Mo(NAr)_2Cl_2(dme) \xrightarrow{b} Mo(NAr)_2(CH_2R)_2 \xrightarrow{c} Mo(NAr)(CHR)(OTf)_2(dme)$$

a) 2 $ArNH_2$, 8 $ClSiMe_3$, 4 Et_3N, dme, 60 °C **b**) 2 RCH_2MgCl, Et_2O **c**) 3 HOTf, dme, -25 °C

Scheme 1.3. General synthesis of molybdenum imido alkylidene bistriflate complexes.

Many molybdenum complexes containing imido ligand variations have been previously synthesized by varying the aniline reagent ($ArNH_2$) used in the first step of this scheme (Table 1.1).[16,23,24,42,56-59] Synthesis of the bis(triflate) complex is not always straightforward. For example, decomposition in the presence of triflic acid was observed for Mo(N-2,6-i-Pr_2-4-

Table 1.1. Variation of Arylimido Ligands in Molybdenum Complexes

$Mo(NR)_2Cl_2(dme)$	$Mo(NR)_2(CH_2R')_2$	$Mo(NR)(CHR')(OTf)_2(dme)$	
R	R'	outcome	references
2,6-i-Pr_2-4-BrC_6H_2	CMe_2Ph	isolated	24
2,6-i-Pr_2-4-CNC_6H_2	CMe_3	decomposed	24
3,5-$Me_2C_6H_3$	CMe_2Ph	isolated	24
2-i-PrC_6H_4	CMe_2Ph	isolated	24
2-$CF_3C_6H_4$	CMe_2Ph	isolated	24
	CMe_3	isolated	42
2-PhC_6H_4 (py adduct)	CMe_3	isolated	24
2,6-$Me_2C_6H_3$	CMe_2Ph	isolated	23, 24
	CMe_3	isolated	24
2-t-BuC_6H_4	CMe_2Ph	isolated	23, 24
	CMe_3	isolated	24
2,6-i-$Pr_2C_6H_3$	CMe_2Ph	isolated	16
	CMe_3	isolated	16
	Ph		23
C_6F_5	CMe_2Ph	decomposed	23
3,5-$(CF_3)_2C_6H_3$	CMe_2Ph	decomposed	23
$(CHMePh)_2C_6H_3$	none reported		58
2,4,6-$Ph_3C_6H_2$	none reported		59
2,6-$Et_2C_6H_3$	CMe_2Ph	isolated	42
2,4-t-Bu-6-$CH_3C_6H_2$	CMe_3	isolated	42
2,6-i-Pr_2-4-FcC_6H_2 (Fc = ferrocenyl)	CMe_2Ph	isolated	57
t-Bu	none reported		23
1-adamantyl	CMe_2Ph	isolated	24
	CMe_3	isolated	56

Table 1.2. Summary of Imido Ligand Variation in Mo(NR)(CHR')(Biphen) and (Biad) Complexes

R	R'	Bisaryloxide	References
2,6-i-$Pr_2C_6H_3$	CMe_2Ph	±-biphen	42
2,6-$Et_2C_6H_3$	CMe_2Ph	±-biphen	42
2,6-$Me_2C_6H_3$	CMe_2Ph	±-biphen	42
1-adamantyl	CMe_2Ph	±-biphen	56
2-t-BuC_6H_4	CMe_2Ph	±-biphen	56
2-t-BuC_6H_4	2-$MeOC_6H_4$	±-biphen	56
2-$CF_3C_6H_4$	CMe_2Ph	±-biphen	42
2-$CF_3C_6H_4$	CMe_3	±-biphen	42
2-$CF_3C_6H_4$	2-$MeOC_6H_4$	±-biphen	42
2,6-i-$Pr_2C_6H_3$	CMe_2Ph	*S*-biphen	40, 42
2,6-$Et_2C_6H_3$	CMe_2Ph	*S*-biphen	41, 42
2,6-$Me_2C_6H_3$	CMe_2Ph	*S*-biphen	42
2-$CF_3C_6H_4$	CMe_2Ph	*S*-biphen	56
2-$CF_3C_6H_4$	CMe_3	*S*-biphen	42
2-$CF_3C_6H_4$	2-$MeOC_6H_4$	*S*-biphen	42
2,4-t-Bu_2-6-MeC_6H_2	CMe_3	*S*-biphen	42
2-$CF_3C_6H_4$	CMe_3	±-biad	42
2,6-$Me_2C_6H_3$	CMe_2Ph	±-biad	42
2,6-i-$Pr_2C_6H_3$	CMe_2Ph	±-biad	42
2,6-$Me_2C_6H_3$	CMe_2Ph	*S*-biad	42
2-$CF_3C_6H_4$	CMe_3	*S*-biad	42
3,5-$Me_2C_6H_3$	CMe_2Ph	*S*-biad	56
2,6-i-$Pr_2C_6H_3$	CMe_2Ph	*S*-biad	42
2,6-$Et_2C_6H_3$	CMe_2Ph	*S*-biad	42

$CNC_6H_2)_2(CH_2CMe_3)_2$, Mo(N$C_6F_5)_2(CH_2CMe_2Ph)_2$ and Mo(N-3,5-$(CF_3)_2C_6H_3)_2(CH_2CMe_2Ph)_2$.

The standard procedure for the reaction of diols with Mo(NAr)(CHR)$(OTf)_2$(dme) is as follows. A THF solution of benzyl potassium is added to the diol in THF until endpoint, as indicated by a light orange color in the solution. The solution of the dipotassium salt of the diol is then added to a THF solution of the molybdenum triflate precursor, and the mixture is stirred. The solvent is then evaporated and the residue is suspended in toluene or benzene and filtered through Celite to remove the potassium triflate byproduct. The resulting solution is then dried *in vacuo* and the residue is crystallized using appropriate solvents. Using many of these known Mo(NAr)(CHR)$(OTf)_2$(dme) starting materials, a series of biphen and biad complexes have been synthesized (Table 1.2).[40-42,56]

This chapter outlines further efforts to examine the effect of imido group variation on the reactivities of ARCM catalysts by studying halogenated imido groups including N-2-IC_6H_4, N-2,4-$F_2C_6H_3$, N-2,4,6-$F_3C_6H_2$, N-2,4,6-$Cl_3C_6H_2$, N-2,6-Br_2-4-$CH_3C_6H_2$ and N-2,6-$Cl_2C_6H_3$.

RESULTS AND DISCUSSION

1.1. Synthesis of Molybdenum Complexes Containing 2-Iodo, 2,4-Difluoro, 2,4,6-Trifluoro and 2,4,6-Trichloroarylimido Ligands

Using 2-iodoaniline, the complex Mo(N-2-$IC_6H_4)_2Cl_2$(dme), **1**, was synthesized as a dark red powder in 51% yield (Scheme 1.3 where NAr = N-2-IC_6H_4). Reaction with neopentylmagnesium chloride generated the dialkyl complex, Mo(N-2-$IC_6H_4)_2(CH_2CMe_3)_2$, **2**, in 94% yield, also as a dark red powder. Subsequent treatment of **2** with triflic acid did not generate the desired Mo(N-2-IC_6H_4)$(CHCMe_3)(OTf)_2$(dme), but instead resulted in decomposition of the complex.

Using 2,4-difluoroaniline, problems were encountered in the first step of the synthetic scheme. The desired product, Mo(N-2,4-$F_2C_6H_3)_2Cl_2$(dme), was not isolated. However, using 2,4,6-trifluoroaniline, Mo(N-2,4,6-$F_3C_6H_2)_2Cl_2$(dme), **3**, was obtained as a dark red powder in

92% yield (Scheme 1.3 where NAr = N-2,4,6-$F_3C_6H_2$). Unfortunately, reaction of **3** with neophyl or neopentylmagnesium chloride yielded dark red oily products that could not be crystallized or purified.

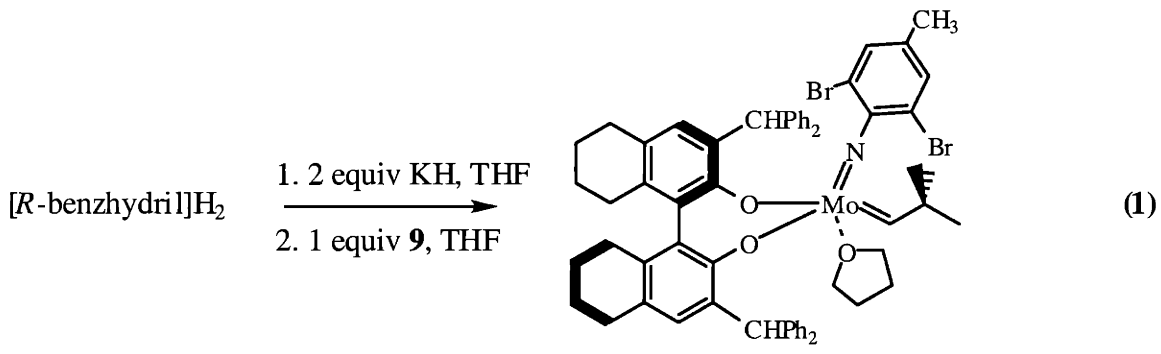
Synthesis of Mo(N-2,4,6-$Cl_3C_6H_2)_2Cl_2$(dme), **4**, yielded the product as a purple-red solid in 87% yield (Scheme 1.3 where NAr = N-2,4,6-$Cl_3C_6H_2$). Reaction of **4** with neophylmagnesium chloride yielded Mo(N-2,4,6-$Cl_3C_6H_2)_2(CH_2CMe_2Ph)_2$, **5**, as an orange powder (77% yield). This product decomposed within hours, forming a white fibrous solid, which was found to be 2,4,6-trichloroaniline. Similar decomposition was observed in the reaction of **4** with neopentylmagnesium chloride that yielded the product Mo(N-2,4,6-$Cl_3C_6H_2)_2(CH_2CMe_3)_2$, **6**. Complexes **4** and **6** were characterized by ^1H and ^{13}C NMR, however elemental analysis was not possible because of decomposition, the mechanism of which is unknown.

1.2. Synthesis of Molybdenum Complexes Containing 2,6-Dibromo-4-methylarylimido Ligands

The syntheses of complexes containing the brominated arylimido ligands, Mo(N-2,6-$Br_2C_6H_3)_2Cl_2$(dme) and Mo(N-2,4,6-$Br_3C_6H_2)_2Cl_2$(dme), were unsuccessful, both yielding red oils consisting of a mixture of unknown products. Tungsten complexes containing the 2,6-dibromo-4-methylarylimido ligand are reported to be highly active ROMP and olefin metathesis catalysts[60] but to the best of our knowledge, the 2,6-dibromo-4-methylarylimido ligand has not been a target of investigation for molybdenum chemistry. Mo(N-2,6-Br_2-4-$CH_3C_6H_2)_2Cl_2$(dme), **7**, was obtained as a dark red powder in 74% yield from the standard reaction conditions using 2,6-dibromo-4-methylaniline (Scheme 1.3 where NAr = N-2,6-Br_2-4-$CH_3C_6H_2$). Reaction of **7** with two equiv neopentylmagnesium chloride gave Mo(N-2,6-Br_2-4-$CH_3C_6H_2)_2(CH_2CMe_3)_2$, **8**, in quantitative yield as a dark red powder. Complex **8** was then reacted with triflic acid to give Mo(N-2,6-Br_2-4-$CH_3C_6H_2$)(CHCMe$_3$)(OTf)$_2$(dme), **9**, as a yellow powder in 85% yield. By ^1H NMR (500 MHz, C_6D_6), complex **9** existed as a ~3:1

mixture of *syn:anti* isomers with the alkylidene proton resonances appearing at 14.96 ppm (Mo=C*H anti*, J_{CH} = 140 Hz) and 14.13 ppm (Mo=C*H syn*, J_{CH} = 120 Hz).

Molybdenum alkylidene bisaryloxide complexes containing the brominated arylimido group were then synthesized. [*S*-Biphen]H_2 was synthesized and resolved by John B. Alexander.[42] Reaction of deprotonated [*S*-biphen]H_2 with **9** gave a dark red oil that showed ^{1}H NMR resonances characteristic of the expected alkylidene product along with other impurities.

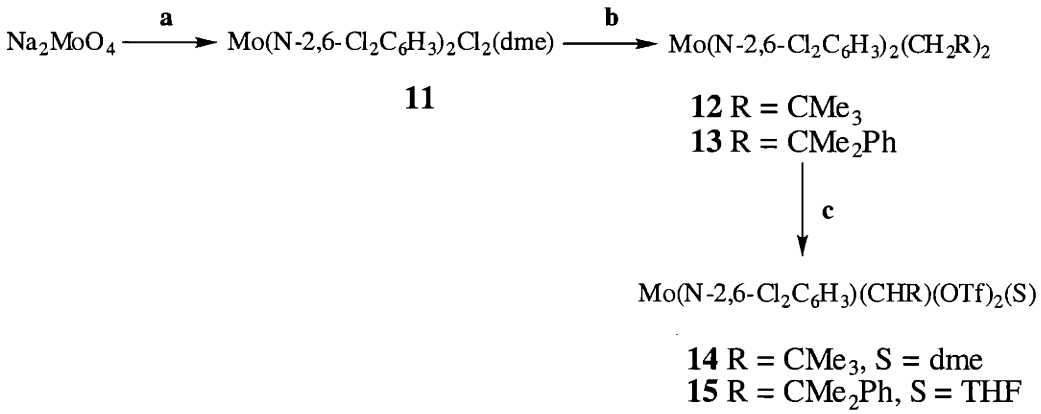


10 **(1)**

However, all attempts to precipitate and purify Mo(N-2,6-Br_2-4-$CH_3C_6H_2$)($CHCMe_3$)(*S*-biphen)(THF) were unsuccessful. [*R*-Benzhydril]H_2 was synthesized by Stephen A. Miller.[47] [*R*-Benzhydril]H_2 was deprotonated and reacted with **9** to give Mo(N-2,6-Br_2-4-$CH_3C_6H_2$)($CHCMe_3$)(*R*-benzhydril)(THF), **10**, as a golden yellow powder in 22% yield (eq 1).

1.3. Synthesis of Molybdenum Complexes Containing 2,6-Dichloroarylimido Ligands

Using 2,6-dichloroaniline (Scheme 1.4), the preparation of Mo(N-2,6-$Cl_2C_6H_3)_2Cl_2$(dme), **11**, was straightforward, giving the product as dark red needles in 94% yield. Two reddish orange dialkyl complexes were then prepared from **11**, each in quantitative yield, the first by reaction with 2 equiv neopentylmagnesium chloride to give Mo(N-2,6-$Cl_2C_6H_3)_2(CH_2CMe_3)_2$, **12**, and the second by reaction with 2 equiv neophylmagnesium chloride to give Mo(N-2,6-$Cl_2C_6H_3)_2(CH_2CMe_2Ph)_2$, **13**.



a) 2 2,6-$Cl_2C_6H_3NH_2$, 8 $ClSiMe_3$, 4 Et_3N, dme, 60 °C **b**) $ClMgCH_2R$ (R = CMe_2, CMe_2Ph), Et_2O

c) 3 HOTf, dme –25 °C

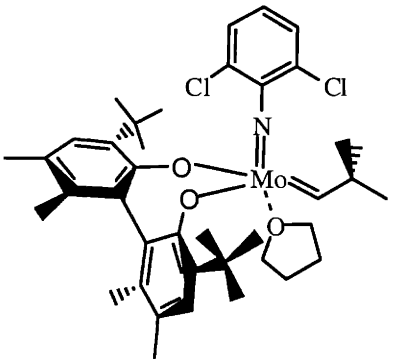
Scheme 1.4. Synthesis of Mo(N-2,6-$Cl_2C_6H_3$)(CHR)$(OTf)_2$(S), 14 (R = CMe_3, S = dme) and 15 (R = CMe_2Ph, S = THF).

Reaction of **12** with triflic acid gave the neopentylidene bis(triflate) complex Mo(N-2,6-$Cl_2C_6H_3$)($CHCMe_3$)$(OTf)_2$(dme), **14**, as a yellow solid in 56% yield. By ^1H NMR (500 MHz, C_6D_6), the product existed as a 1:4 mixture of the *anti*:*syn* isomers with the *anti* alkylidene proton resonance at 14.98 ppm and the *syn* at 14.08 ppm (J_{CH} = 121 Hz). It was important that any solvent be completely removed at each drying step to prevent anilinium triflate from being extracted along with the desired product.

Reaction of **13** with triflic acid proved to be a difficult method for the synthesis of Mo(N-2,6-$Cl_2C_6H_3$)($CHCMe_2Ph$)$(OTf)_2$(dme) because the desired product could not be adequately separated from anilinium triflate impurities. In one case, after standard workup, a brown solid was obtained and triturated with THF to give a yellow solid that was insoluble in all other solvents. By ^1H NMR (500 MHz, THF-d_8), the product was shown to be a mixture of the two diastereomeric THF adducts of the neophylidene product, Mo(N-2,6-$Cl_2C_6H_3$)($CHCMe_2Ph$)$(OTf)_2(THF)_x$, **15**, with two singlets corresponding to each diastereomeric *syn* alkylidene proton at 14.21 ppm (J_{CH} = 126 Hz) and 14.17 ppm (J_{CH} = 124 Hz).

By ^{19}F NMR (282 MHz, THF-d_8), four singlets were observed at –80.14, –80.52, –81.10 and –81.33 ppm corresponding to two inequivalent triflate CF_3 groups per molybdenum complex. In the solid state, elemental analysis confirmed that the complex existed as a mono(THF) adduct. The isolated yield of this product was 26%. As a result of the inherent difficulties found in the reproducible synthesis of purified Mo(N-2,6-$Cl_2C_6H_3$)(CHCMe$_2$Ph)(OTf)$_2$(dme), this complex was not targeted as a precursor to ARCM catalysts.

The reproducible synthesis of **14** made this a good precursor for the synthesis of ARCM catalysts of the type Mo(N-2,6-$Cl_2C_6H_3$)(CHCMe$_3$)(bisaryloxide). [*S*-Biphen]H_2 was deprotonated and reacted with **14** to give Mo(N-2,6-$Cl_2C_6H_3$)(CHCMe$_3$)(*S*-biphen)(THF), **16**, as ruby red crystals in 55% yield (eq 2). Using the same procedure, the analogous product containing [±-biphen]H_2, Mo(N-2,6-$Cl_2C_6H_3$)(CHCMe$_3$)(±-biphen)(THF), **16rac**, was also synthesized.

[*S*-biphen]H_2 $\xrightarrow[\text{2. 1 equiv } \mathbf{14}\text{, THF}]{\text{1. 2 equiv PhCH}_2\text{K, THF}}$  (2)

16

By ^1H NMR (500 MHz, toluene-d_8), **16** exists only as the *syn* alkylidene isomer with the resonance corresponding to the Mo=C*H* proton occurring at 11.33 ppm (J_{CH} = 120 Hz). When the solution is cooled to -80 °C (Figure 1.1), this resonance splits into two peaks of equal intensity at 13.24 (J_{CH} = 120 Hz) and 11.12 ppm. Based on coupling constants and chemical shifts, the resonance at 11.12 ppm is assigned as the THF-free complex *syn*-Mo(N-2,6-$Cl_2C_6H_3$)(CHCMe$_3$)(*S*-biphen) while the downfield resonance at 13.24 ppm corresponds to the THF-coordinated *syn* species, **16**. When the sample is heated, the THF dissociates from the complex, as evidenced by the ^1H NMR spectrum at +50 °C in which the Mo=C*H* resonance is

shifted upfield to 11.12 ppm (the same chemical shift as found for the resonance at -80 °C for the THF-free species).

The ^{1}H NMR spectra of **16** in THF-d_8 (Figure 1.2) show that at room temperature, there are Mo=C*H* resonances for both the *syn* and *anti* THF adduct complexes (12.91 ppm with J_{CH} = 120 Hz and 14.12 ppm, respectively) in a ratio of ~7:1. When the sample is cooled to -40 °C there is no significant change in the chemical shifts of these resonances, with the *syn* and *anti* resonances appearing at 12.96 and 14.18 ppm, respectively, in a 10:1 ratio.

The molecular structure of **16** was determined by Peter J. Bonitatebus, Jr. by X-ray crystallographic study of single crystals of the complex. Crystallographic data, collection parameters and refinement parameters are given in Table 1.3, while selected bond lengths (Å) and angles (°) are given in Table 1.4. The molecular structure and atom-labeling scheme are shown in Figure 1.3. Crystals of **16** were grown from a concentrated ether solution at −30 °C. The catalyst crystallized in the $P2_12_12_1$ orthorhombic space group as a five-coordinate molybdenum imido *syn*-alkylidene biphenoxide THF complex. The complex is a distorted trigonal bipyramid with the THF (O(3)) and one biphenolate oxygen (O(1)) occupying the axial positions.

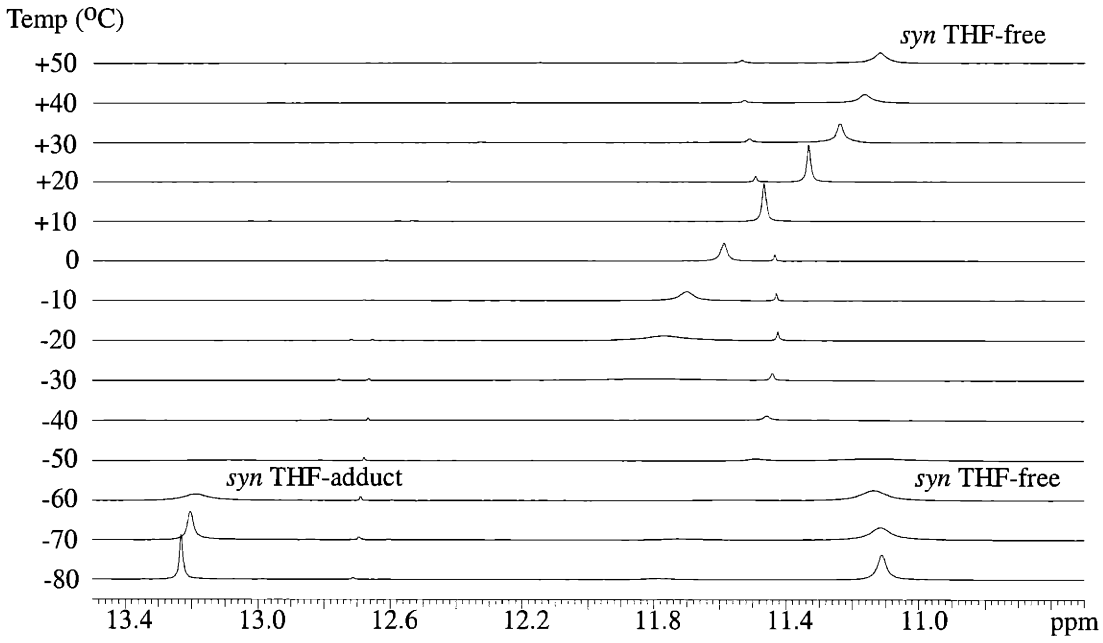


Figure 1.1. Variable temperature ^{1}H NMR spectra (500 MHz, toluene-d_8) of the alkylidene proton region for Mo(N-2,6-$Cl_2C_6H_3$)(CHCMe$_3$)(*S*-biphen)(THF), 16.

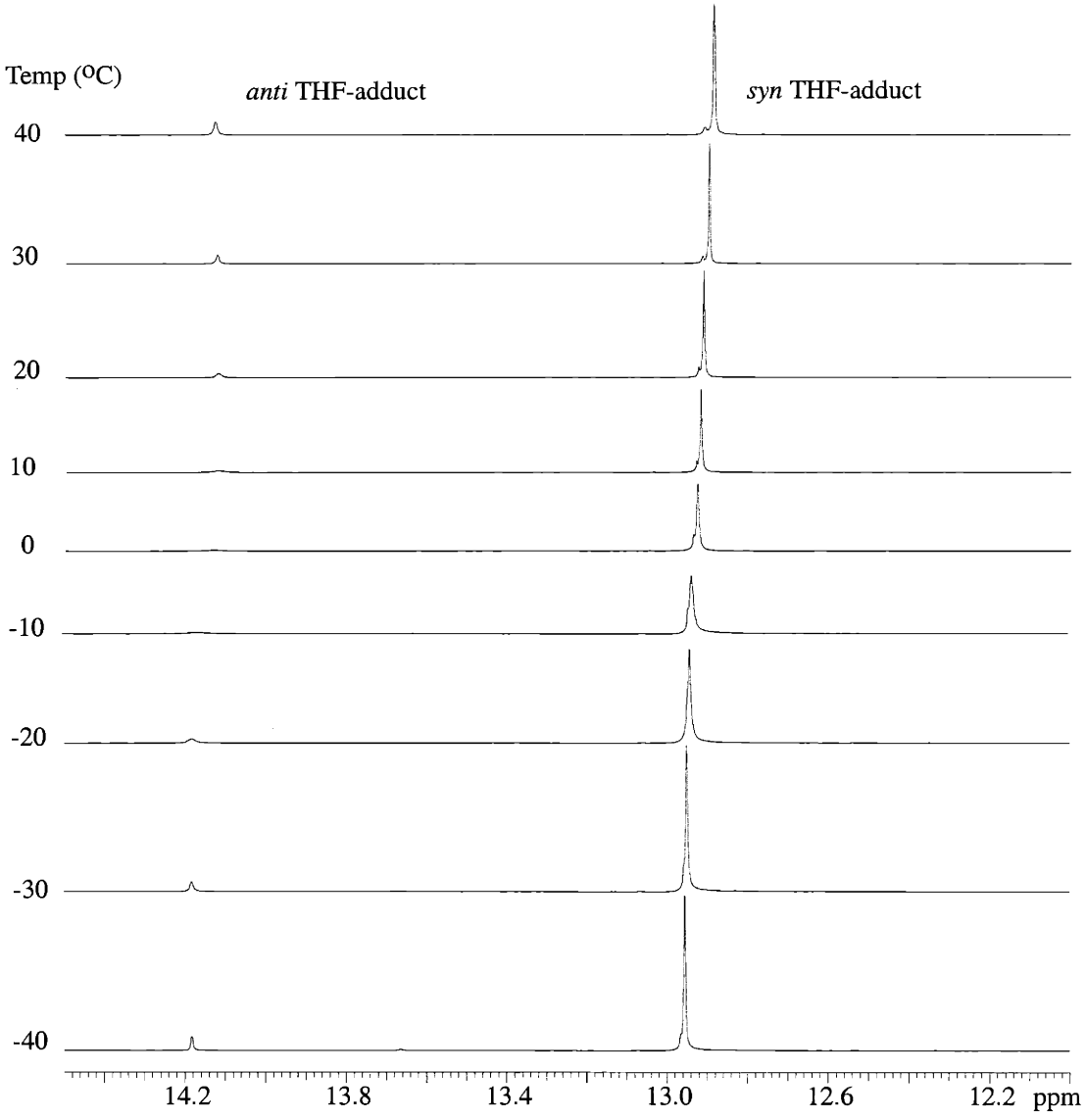


Figure 1.2. Variable temperature ^{1}H NMR spectra (500 MHz, THF-d_8) of the alkylidene proton region for Mo(N-2,6-$Cl_2C_6H_3$)(CHCMe$_3$)(*S*-biphen)(THF), 16.

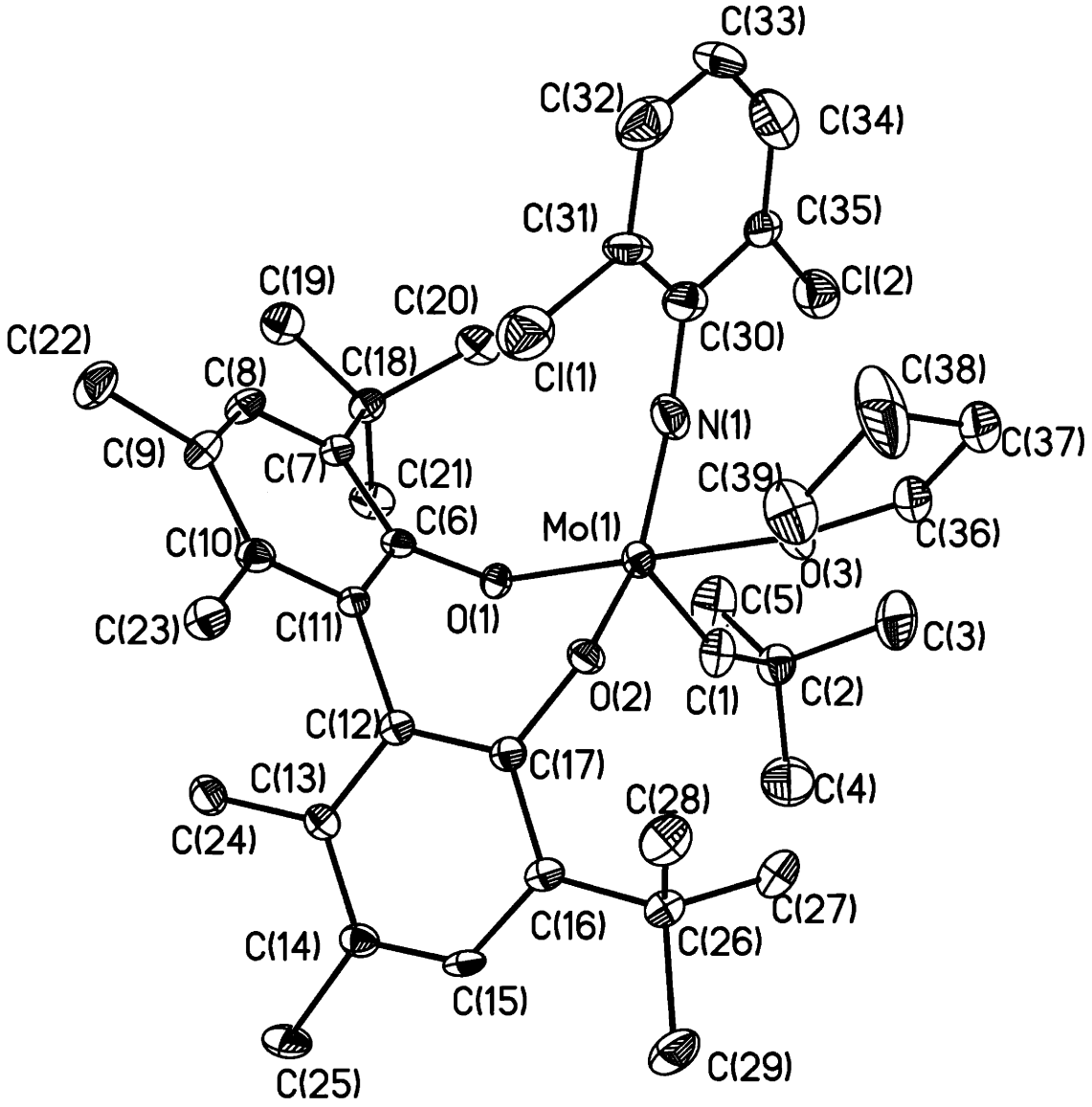
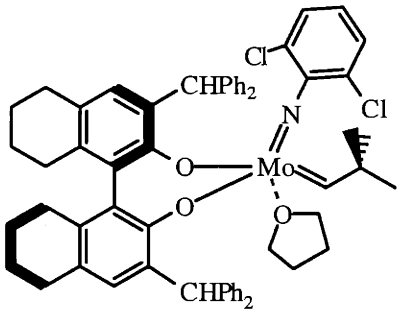


Figure 1.3. ORTEP of Mo(N-2,6-$Cl_2C_6H_3$)(CHCMe_3)(*S*-biphen)(THF), 16.

[*R*-Benzhydril]H_2 was deprotonated and reacted with **14** to give Mo(N-2,6-$Cl_2C_6H_3$)($CHCMe_3$)(*R*-benzhydril)(THF), **17**, as a golden yellow powder in 47% yield (eq 3).

[*R*-benzhydril]H_2 —(1. 2 equiv KH, THF; 2. 1 equiv **14**, THF)→ 

17 (3)

By ^{1}H NMR in C_6D_6, **17** exists only as the *syn* THF adduct with a Mo=C*H* resonance at 12.51 ppm (J_{CH} = 121 Hz). Variable temperature ^{1}H NMR spectra were obtained for **17** in THF-d_8 (Figure 1.4) and at room temperature there are resonances corresponding to the *syn* and *anti* THF adducts at 12.28 (J_{CH} = 121 Hz) and 14.27 ppm, respectively, in a ratio of 17:1. When the sample is cooled to -40 °C, the resonance corresponding to the *syn* THF adduct shifts upfield to 12.08 ppm (J_{CH} = 122 Hz) and the resonance for the *anti* THF adduct shifts slightly to 14.29 ppm. The ratio of the two resonances does not change.

The molecular structure of **17** was determined by James P. Araujo and Paula L. Diaconescu by X-ray crystallographic study of single crystals of the complex that were grown over several days from a concentrated ether and THF solution at −30 °C. The crystals were square, pale yellow plates. Crystallographic data, collection parameters and refinement parameters are given (Table 1.3), as are selected bond lengths (Å) and angles (°) (Table 1.4). The molecular structure and atom-labeling scheme are shown in the accompanying ORTEP diagram (Figure 1.5). The catalyst crystallized in the $P2_12_12_1$ orthorhombic space group. As shown in Table 1.4, bond lengths and angles were comparable to those for complex **16**.

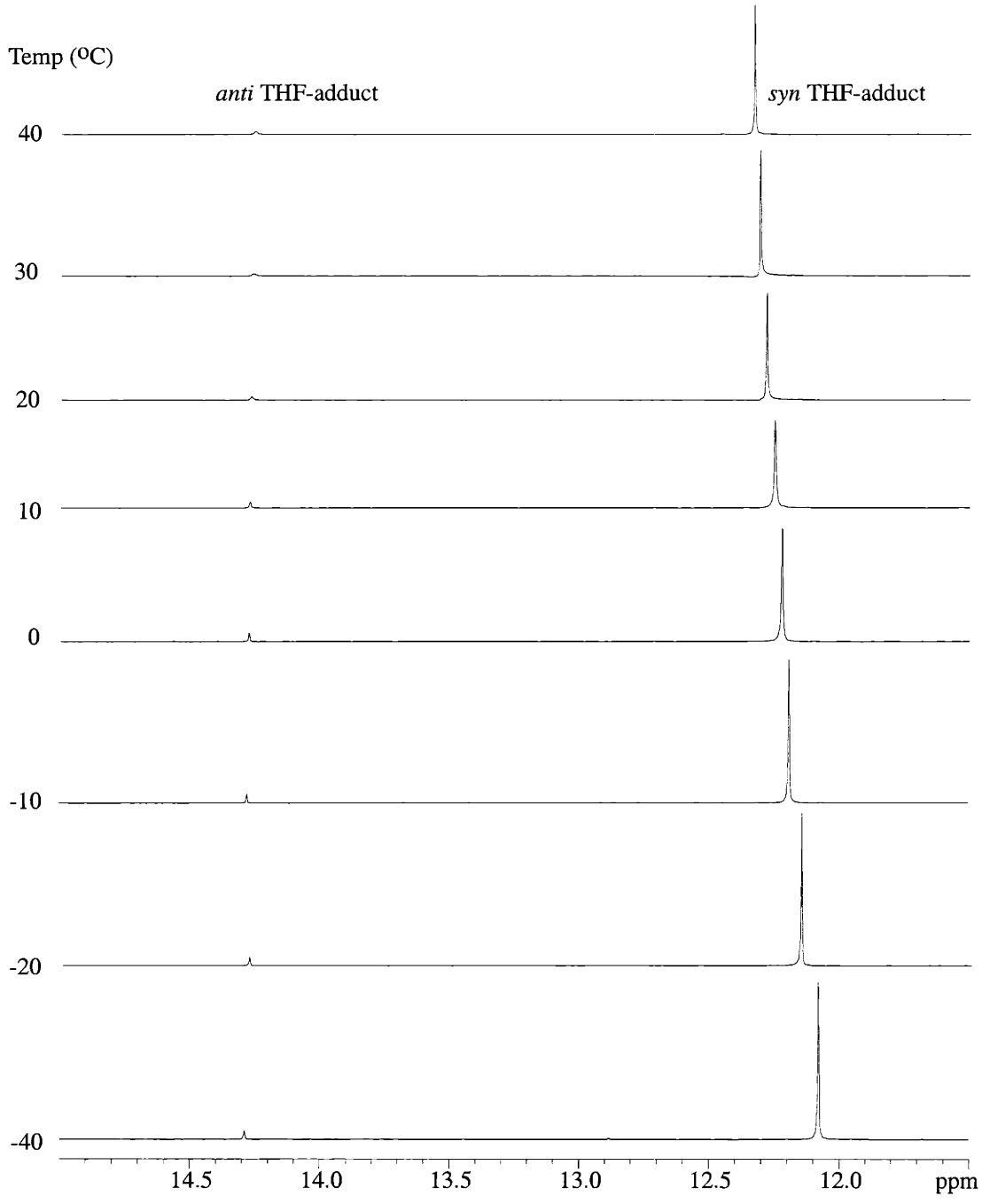


Figure 1.4. Variable temperature ^{1}H NMR spectra (500 MHz, THF-d_8) of the alkylidene proton region for Mo(N-2,6-$Cl_2C_6H_3$)(CHCMe$_3$)(*R*-benzhydril)(THF), 17.

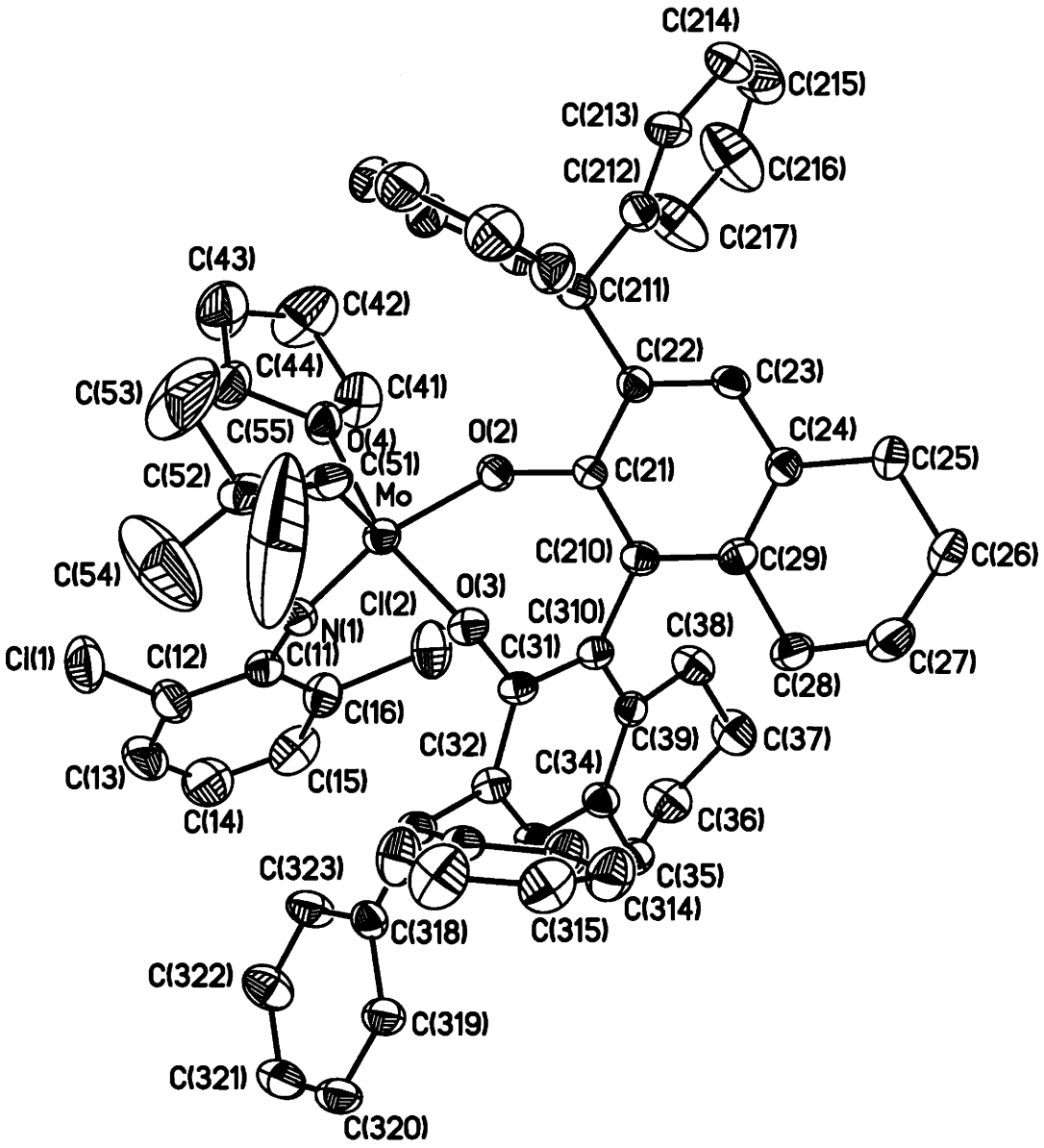


Figure 1.5. ORTEP of Mo(N-2,6-$Cl_2C_6H_3$)(CHCMe$_3$)(*R*-benzhydril)(THF), 17.

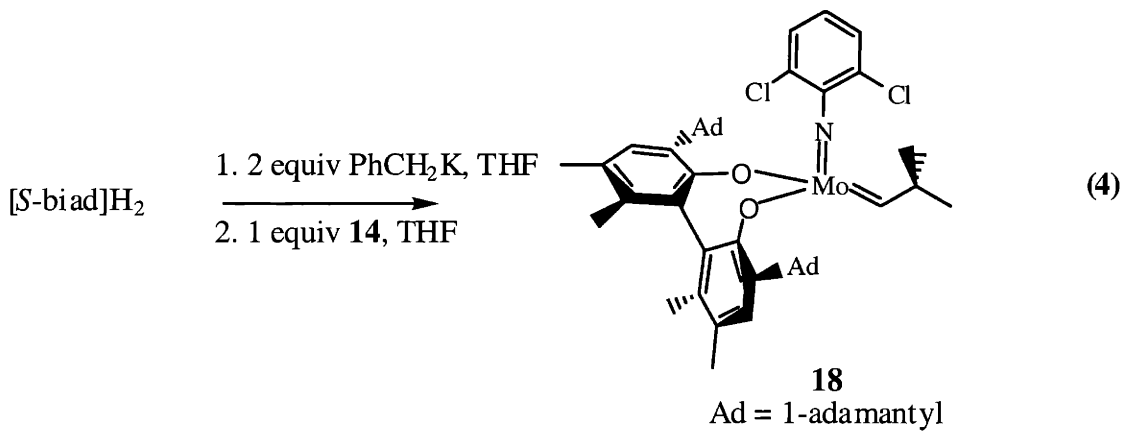
Table 1.3. Crystallographic Data, Collection Parameters, and Refinement Parameters for Mo(N-2,6-$Cl_2C_6H_3$)(CHCMe$_3$)(*S*-biphen)(THF) (16) and Mo(N-2,6-$Cl_2C_6H_3$)(CHCMe$_3$)(*R*-benzhydril)(THF) (17).

	(*S*-biphen) **16**	(*R*-benzhydril) **17**
Empirical formula	$MoC_{39}H_{53}NO_3Cl_2$	$MoC_{61}H_{61}NO_3Cl_2$
Formula weight	750.66	1022.95
Temperature	293(2) K	183(2) K
Wavelength	0.71073 Å	0.71073 Å
Crystal system, space group	Orthorhombic	Orthorhombic
	$P2_12_12_1$	$P2_12_12_1$
Unit cell dimensions	a = 10.5365(6) Å.	13.773(5) Å
	b = 18.3753(11) Å	17.182(6) Å
	c = 19.7029(12) Å	21.696(8) Å
	$\alpha = 90°$	90°
	$\beta = 90°$	90°
	$\gamma = 90°$	90°
Volume	3814.7(4) Å^3	5134(3) Å^3
Z, Calculated density	4, 1.307 Mg/m^3	4, 1.323 Mg/m^3
Absorption coefficient	0.520 mm^{-1}	0.406 mm^{-1}
F(000)	1576	2136
Theta range for data collection	2.19 to 23.29°	2.11 to 23.30°
Limiting indices	$-11 \le h \le 11$	$-6 \le h \le 15$
	$-20 \le k \le 15$	$-18 \le k \le 19$
	$-21 \le l \le 21$	$-24 \le l \le 24$
Reflections collected / unique	15643 / 5473	21131 / 7382
	[R_{int} = 0.0387]	[R_{int} = 0.0552]
Completeness to theta = 23.29	99.7 %	99.5%
Absorption correction	Empirical	Empirical
Max. and min. transmission	0.2670 and 0.2316	0.9760 and 0.9342
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5473 / 0 / 415	7382 / 0 / 613
Goodness-of-fit on F2	1.044	1.027
Final R indices [I>2((I)]	R1 = 0.0502	R1 = 0.0435
	wR2 = 0.1243	wR2 = 0.0994
R indices (all data)	R1 = 0.0567	R1 = 0.0520
	wR2 = 0.1280	wR2 = 0.1034
Absolute structure parameter	0.01(6)	-0.06(4)
Largest diff. peak and hole	0.838 and -0.551 e.A^{-3}	0.492 and -0.322 e.A^{-3}

Table 1.4. Selected bond lengths (Å) and angles (°) for Mo(N-2,6-$Cl_2C_6H_3$)($CHCMe_3$)(*S*-biphen)(THF) (16) and Mo(N-2,6-$Cl_2C_6H_3$)($CHCMe_3$)(*R*-benzhydril)(THF) (17).

		(*S*-biphen), **16**		(*R*-benzhydril), **17**
$Mo\text{-}N_{imido}$	Mo-N(1)	1.745(6)	Mo-N(1)	1.757(4)
$Mo\text{-}C_{alkylidene}$	Mo-C(1)	1.872(7)	Mo-C(51)	1.898(5)
$Mo\text{-}O_{biphen}$	Mo-O(1)	1.998(3)	Mo-O(2)	1.950(3)
$Mo\text{-}O_{biphen}$	Mo-O(2)	1.961(3)	Mo-O(3)	2.006(3)
$Mo\text{-}O_{THF}$	Mo-O(3)	2.266(4)	Mo-O(4)	2.232(3)
$O_{biphen}\text{-}C_{aryl}$	O(1)-C(6)	1.354(7)	O(2)-C(21)	1.378(5)
$O_{biphen}\text{-}C_{aryl}$	O(2)-C(17)	1.378(7)	O(3)-C(31)	1.361(5)
$C_{alkylidene}\text{-}CMe_3$	C(1)-C(2)	1.451(9)	C(51)-C(52)	1.491(7)
$N_{imido}\text{-}C_{aryl}$	N(1)-C(30)	1.355(9)	N(1)-C(11)	1.393(6)
$N_{imido}\text{-}Mo\text{-}C_{alkylidene}$	N(1)-Mo-C(1)	107.0(3)	N(1)-Mo-C(51)	108.6(2)
Mo=C-C	Mo-C(1)-C(2)	150.3(6)	Mo-C(51)-C(52)	143.5(4)
$Mo{=}N\text{-}C_{imido}$	Mo-N(1)-C(30)	149.8(6)	Mo-N(10)-C(11)	152.1(3)
$O_{biphen}\text{-}Mo\text{-}O_{biphen}$	O(2)-Mo(1)-O(1)	95.58(16)	O(2)-Mo-O(3)	88.89(12)

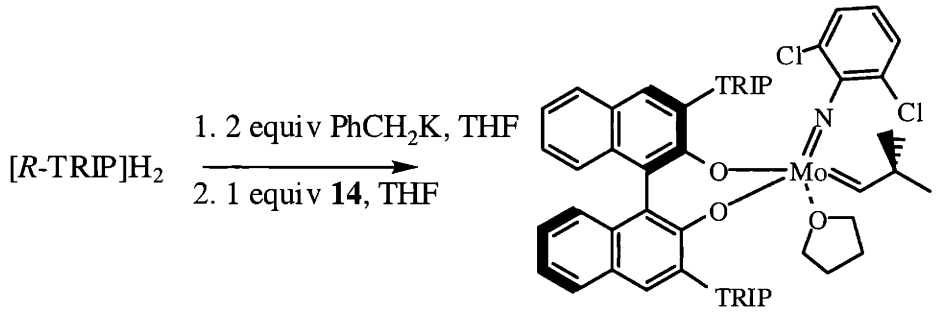
Preparation of the *S*-biad analogue of these dichloroarylimido complexes was also straightforward. [*S*-Biad]H_2 was prepared and resolved by John B. Alexander and Jeffrey H. Houser.[42] Deprotonation of [*S*-biad]H_2 followed by addition to the bistriflate **14** gave Mo(N-2,6-$Cl_2C_6H_3$)($CHCMe_3$)(*S*-biad), **18**, as ruby colored crystals in 61% yield (eq 4). By ^1H NMR (500 MHz, C_6D_6), the product exists as a four-coordinate, THF-free complex with only the *syn* alkylidene proton appearing at 11.05 ppm (J_{CH} = 122 Hz).



18
Ad = 1-adamantyl

(4)

Synthesis of Mo(N-2,6-$Cl_2C_6H_3$)($CHCMe_3$)(*R*-TRIP)(THF), **19**, was achieved by addition of deprotonated [*R*-TRIP]H_2 to **14** to give the product as a yellow powder in 49% yield (eq 5). [*R*-TRIP]H_2 was prepared by S. Sherry Zhu.[43] By ^{1}H NMR (500 MHz, C_6D_6), the product exists as a five-coordinate THF adduct. The resonance corresponding to the *syn* alkylidene proton appears at 13.24 ppm (J_{CH} = 121 Hz) in C_6D_6 while the *anti* isomer was not observed.



19
TRIP = 2,4,6-i-$Pr_3C_6H_2$

(5)

By variable temperature ^{1}H NMR in toluene-d_8 (Figure 1.6), the spectrum of **19** at room temperature shows Mo=C*H* resonances for both the *syn* and *anti* THF adducts (13.15 ppm with J_{CH} = 121 Hz and 13.90 ppm, respectively) in a ratio of 16:1. When the sample is cooled to -40

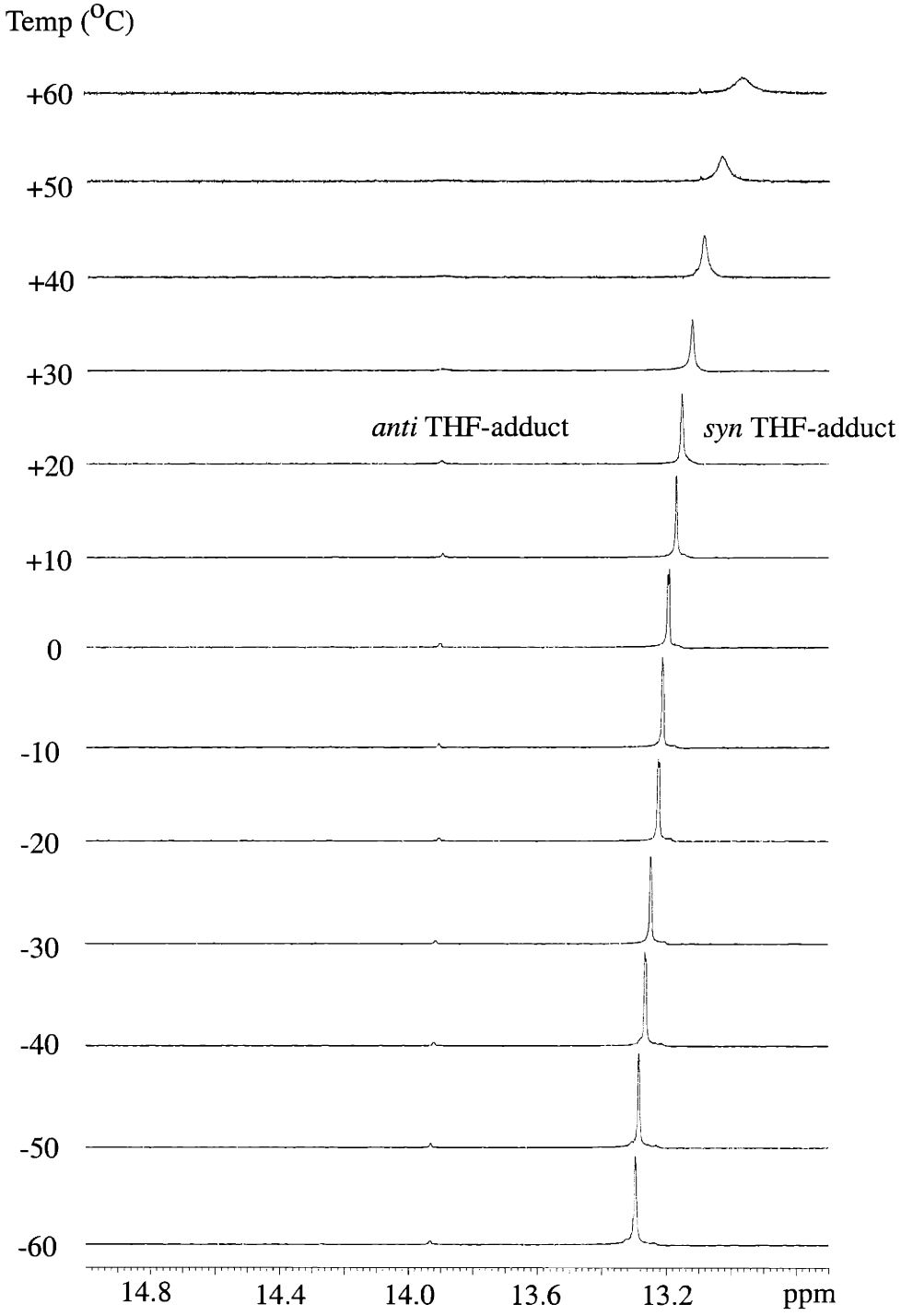
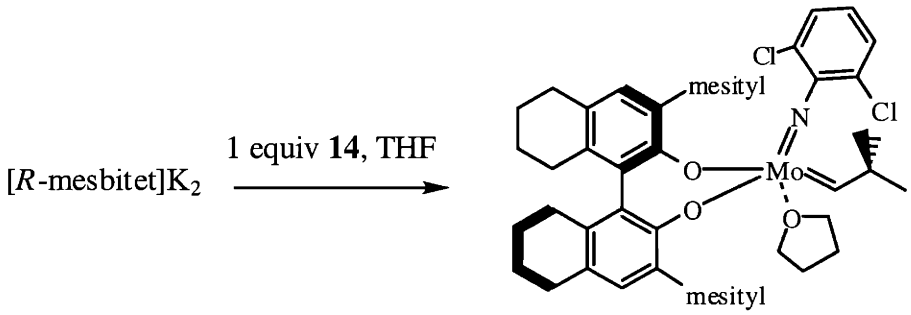


Figure 1.6. Variable temperature ^{1}H NMR spectra (500 MHz, toluene-d_8) of the alkylidene proton region for Mo(N-2,6-$Cl_2C_6H_3$)(CHCMe$_3$)(*R*-TRIP)(THF), 19.

°C there is only a slight change in the chemical shifts of these resonances, with the *syn* and *anti* resonances appearing at 13.26 and 13.92 ppm, respectively, in a 26:1 ratio. When the sample is heated to +60 °C, the Mo=C*H* resonances broaden due to THF dissociation and only the *syn* Mo=C*H* resonance appears at 12.98 ppm.

The behavior of **19** in the presence of excess THF was also examined using variable temperature ^{1}H NMR spectra of the species in THF-d_8 (Figure 1.7). At room temperature, the only significant species present is the *syn* THF adduct with a Mo=C*H* resonance at 13.22 ppm. There are also very minor amounts (<1%) of what appear to be one minor *syn* alkylidene resonance at 13.26 ppm and two *anti* alkylidene Mo=C*H* resonances at 14.00 and 14.30 ppm, based on chemical shifts. Most likely these small resonances correspond to the two diastereomeric THF adducts of the *anti* isomer and the minor diastereomer of the *syn* adduct. When the sample was cooled to -80 °C, there was no significant change in the ^{1}H NMR spectrum, with the major species still being the *syn* THF adduct (13.29 ppm). When heated to +40 °C, the spectrum was still essentially unchanged, with the predominant *syn* THF adduct resonance at 13.22 ppm.

[*R*-Mesbitet]K_2 was synthesized by Sarah J. Dolman.[47] [*R*-Mesbitet]K_2 was added to **14** to give Mo(N-2,6-$Cl_2C_6H_3$)(CHCMe$_3$)(*R*-mesbitet)(THF), **20**, in 41% yield as orange-yellow crystals (eq 6). By ^{1}H NMR (500 MHz, C_6D_6), **20** exists as the THF-coordinated *syn* isomer in solution, with the alkylidene proton resonance Mo=C*H* occurring at 12.89 ppm (J_{CH} = 121 Hz).



(6)

20

mesityl = 2,4,6-$Me_3C_6H_2$

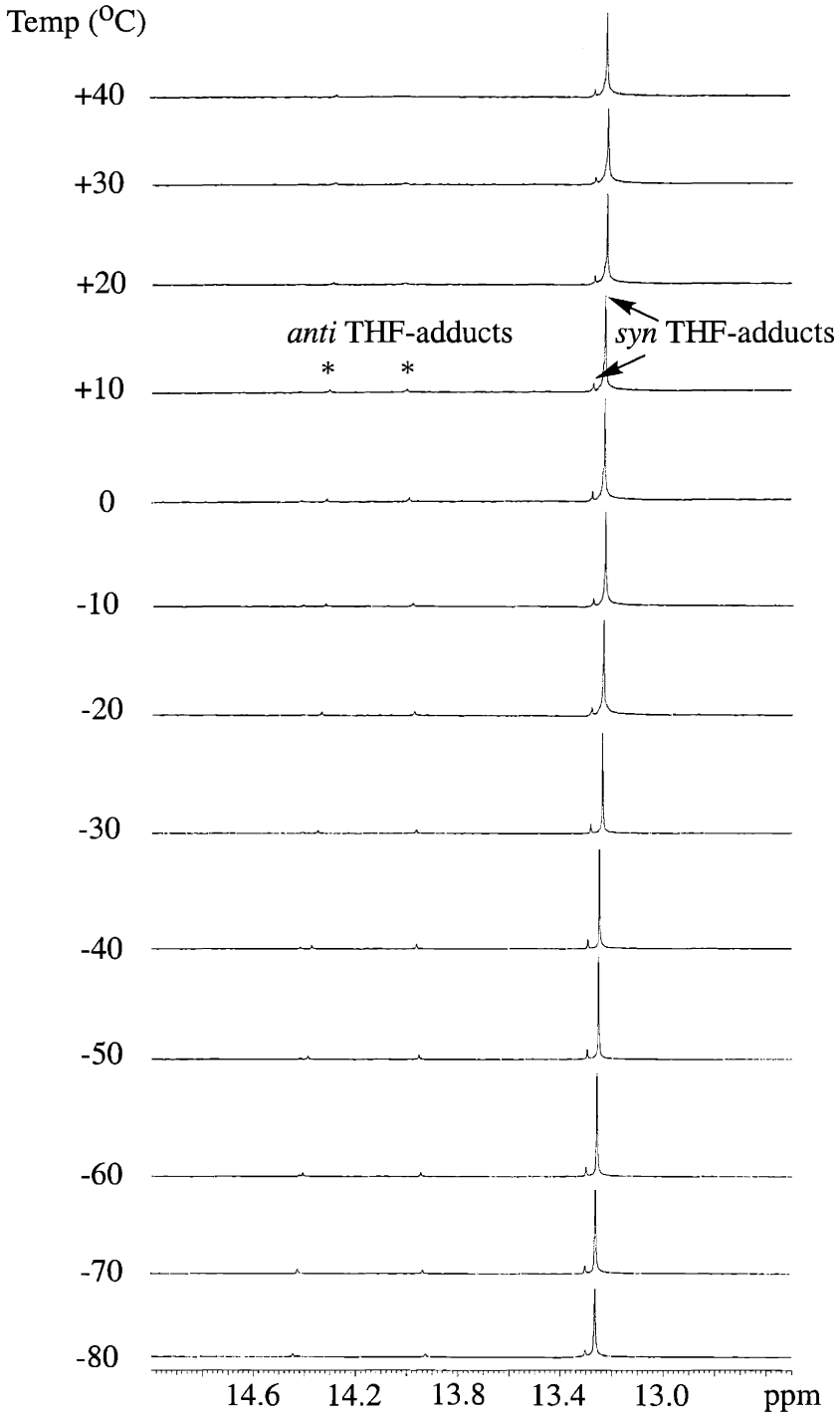


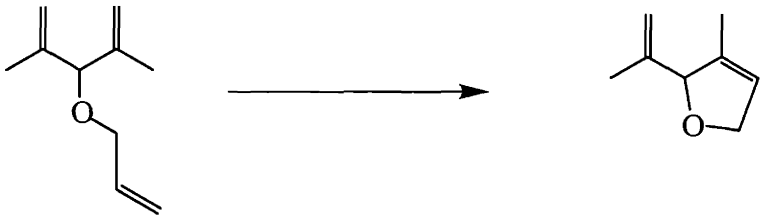
Figure 1.7. Variable temperature ^{1}H NMR spectra (500 MHz, THF-d_8) of the alkylidene proton region for Mo(N-2,6-$Cl_2C_6H_3$)(CHCMe$_3$)(*R*-TRIP)(THF), 19.

1.4. Asymmetric Ring-Closing Metathesis Reactions with Halogenated Arylimido Catalysts

In order to evaluate catalysts containing halogenated arylimido ligands, two triene desymmetrization substrates were used as standards for determining ARCM reactivity, 3-(2,4-dimethylpentadienyl)allyl ether, **21**, and (3,5-dimethyl-(2*E*,5*E*)-heptadienyl)allyl ether, **22**.[41] Substrate **21** ring-closes to give heterocyclic product, 2-*iso*-propenyl-3-methyl-2,5-dihydrofuran, **23**, while **22** ring-closes to give 2-(2*E*-*sec*-butenyl)-3-methyl-2,5-dihydrofuran, **24**. A summary of results for these reactions is shown in Tables 1.5 and 1.6 along with comparative results obtained with other ARCM catalysts.[41,43,56] In all cases, the substrate was diluted in C_6D_6 to give a ~0.2 M solution which was then added to 5 mol% catalyst. Reactions were performed under an atmosphere of nitrogen in the glovebox and each solution was stirred for ~1h at room temperature in a loosely capped vial. The conversion of starting material to ring-closed product was then determined by ^{1}H NMR (500 MHz), using integration of the olefinic proton resonances. No intermolecular cross-coupling of two substrate molecules to give dimeric product was observed in any case. The volatile products were then isolated by vacuum transfer from the metal compounds and analyzed by gas-liquid chromatography using a chiral column (CHIRALDEX-GTA column by Alltech; 90 °C oven temperature) to determine enantiomeric excesses (% ee). A stereochemical proof performed by Daniel S. La of Boston College confirmed that the *R*-configuration of ring-closed product is obtained from catalysts containing *S*-bisaryloxides.[41]

As shown in Tables 1.5 and 1.6, catalysts **10**, and **16**-**20** were all very efficient, each leading to essentially complete conversion to ring-closed product within 1h for both desymmetrization substrates. The optical purity (% ee) of the products was also encouraging, at least 85-100% in all cases except for Mo(N-2,6-$Cl_2C_6H_3$)(CHCMe$_3$)(*S*-biad), **18**, which gave racemic ring-closed product in both reactions. Catalyst **18** was not studied further for this reason. The catalyst containing the brominated arylimido ligand, Mo(N-2,6-Br_2-4-$CH_3C_6H_2$)(CHCMe$_3$)(*R*-benzhydril)(THF), **10**, showed excellent enantioselectivities in both reactions. Further ARCM studies with **10** were not pursued, however, because the synthesis of

Table 1.5. Desymmetrization of 21 with Mo catalysts in benzene at room temperature.[a]

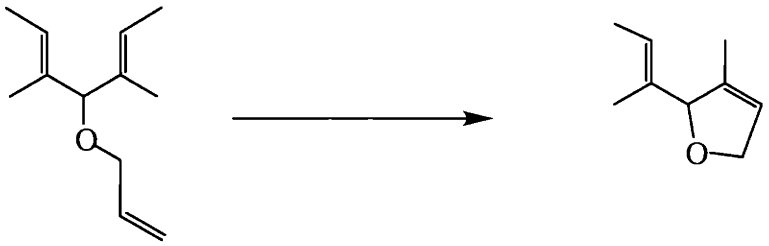


21 **23**

Catalyst	**Time (h)**	**Loading (mol %)**	**Conv**[b]	**ee of 23, config.**[c]
Mo(N-2,6-Br_2-4-$CH_3C_6H_2$)($CHCMe_3$)(*R*-benzhydril)(THF) (**10**)				
	1	5	100%	99%, *S*
Mo(N-2,6-$Cl_2C_6H_3$)($CHCMe_3$)(*S*-biphen)(THF) (**16**)	1	5	100%	90%, *R*
Mo(N-2,6-$Cl_2C_6H_3$)($CHCMe_3$)(*R*-benzhydril)(THF) (**17**)	1	5	100%	95%, *S*
Mo(N-2,6-$Cl_2C_6H_3$)($CHCMe_3$)(*S*-biad) (**18**)	1	5	100%	0%
Mo(N-2,6-$Cl_2C_6H_3$)($CHCMe_3$)(*R*-TRIP)(THF) (**19**)	1	5	100%	86%, *S*
Mo(N-2,6-$Cl_2C_6H_3$)($CHCMe_3$)(*R*-mesbitet)(THF)(**20**)	1	5	100%	90%, *S*
Mo(N-2,6-i-$Pr_2C_6H_3$)($CHCMe_2Ph$)(*S*-biphen)	6	1	94%	93%, *R*
Mo(N-2,6-$Me_2C_6H_3$)($CHCMe_2Ph$)(*S*-biphen)	6	1	93%	93%, *R*
Mo(N-2,6-i-$Pr_2C_6H_3$)($CHCMe_2Ph$)(*S*-biad)	23	5	16%	51%, *R*

[a] Conditions: 0.2M **21** in C_6D_6, N_2 atm, room temperature. [b] Conversion determined by analysis of 500 MHz ^1H NMR of unpurified reaction mixture. [c] Enantioselectivity determined by GLC analysis (CHIRALDEX-GTA by Alltech) in comparison with authentic racemic material.

Table 1.6. Desymmetrization of 22 with Mo catalysts in benzene at room temperature.[a]



22 **24**

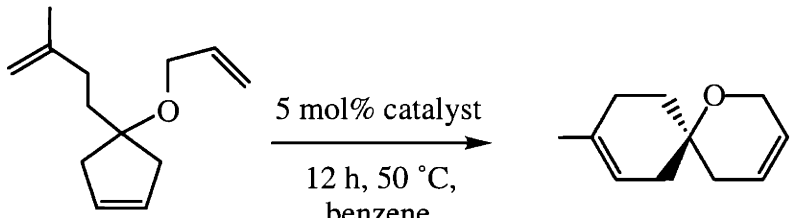
Catalyst	**Time (h)**	**Loading (mol %)**	**Conv**[b]	**ee of 24, config.**[c]
Mo(N-2,6-Br_2-4-$CH_3C_6H_2$)($CHCMe_3$)(*R*-benzhydril)(THF) (**10**)				
	1	5	100%	87%, *S*
Mo(N-2,6-$Cl_2C_6H_3$)($CHCMe_3$)(*S*-biphen)(THF) (**16**)	1	5	100%	97%, *R*
Mo(N-2,6-$Cl_2C_6H_3$)($CHCMe_3$)(*R*-benzhydril)(THF) (**17**)	1	5	100%	91%, *S*
Mo(N-2,6-$Cl_2C_6H_3$)($CHCMe_3$)(*S*-biad) (**18**)	1	5	100%	0%
Mo(N-2,6-$Cl_2C_6H_3$)($CHCMe_3$)(*R*-TRIP)(THF) (**19**)	1	5	100%	91%, *S*
Mo(N-2,6-$Cl_2C_6H_3$)($CHCMe_3$)(*R*-mesbitet)(THF)(**20**)	1	5	100%	96%, *S*
Mo(N-2,6-i-$Pr_2C_6H_3$)($CHCMe_2Ph$)(*S*-biphen)	9	1	32%	94%, *R*
Mo(N-2,6-$Me_2C_6H_3$)($CHCMe_2Ph$)(*S*-biphen)	4	1	>95%	99%, *R*
Mo(N-2,6-i-$Pr_2C_6H_3$)($CHCMe_2Ph$)(*S*-biad)	24	5	10%	33%, *R*
Mo(N-2,6-i-$Pr_2C_6H_3$)($CHCMe_2Ph$)(*R*-TRIP)(THF)	18	5	<5%	n/a
Mo(N-2,6-$Me_2C_6H_3$)($CHCMe_2Ph$)(*R*-TRIP)(THF)	18	5	80%	89%, *S*

[a] Conditions: 0.2M **22** in C_6D_6, N_2 atm, room temperature. [b] Conversion determined by analysis of 500 MHz ^1H NMR of unpurified reaction mixture. [c] Enantioselectivity determined by GLC analysis (CHIRALDEX-GTA by Alltech) in comparison with authentic racemic material.

this catalyst consistently gave low yields of isolated product. Most promising in the desymmetrization reactions were catalysts **16**, **17**, **19** and **20**, containing the 2,6-dichloroarylimido ligand and [*S*-biphen], [*R*-benzhydril], [*R*-TRIP] and [*R*-mesbitet] ligands, respectively. These catalysts gave results for the conversion to ring-closed product and product % ee that were comparable, if not better, than known catalysts. In particular, these catalysts appear to be among the first to provide consistently high enantioselectivities *and* complete conversion within an hour for both ring-closing reactions of **21** and **22**.

In work performed by our collaborators in the Hoveyda group at Boston College, catalysts containing the 2,6-dichloroarylimido ligand were shown to equal or surpass the performance of other ARCM catalysts with many substrates. The catalytic enantioselective synthesis of spirocycle **25** in the presence of 5 mol% Mo(N-2,6-$Cl_2C_6H_3$)(CHCMe$_3$)(*R*-TRIP)(THF), **19**, at 50 °C surpassed the performance of all other catalysts screened, generating

Table 1.7. Enantioselective synthesis of spirocycle 25.



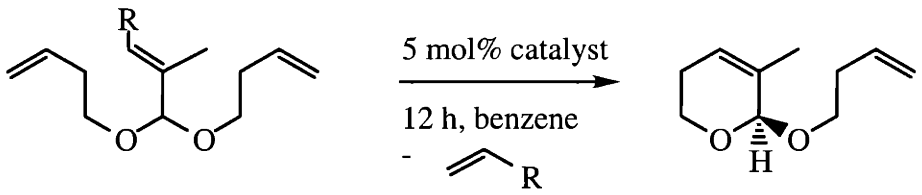
25

catalyst	Conv[a]	% ee[b]
Mo(N-2,6-i-$Pr_2C_6H_3$)(CHCMe$_2$Ph)(*S*-biphen)	100%	51%
Mo(N-2,6-i-$Pr_2C_6H_3$)(CHCMe$_2$Ph)(*R*-TRIP)(THF)	50%	73%
Mo(N-2,6-$Cl_2C_6H_3$)(CHCMe$_3$)(*R*-TRIP)(THF), **19**	84%	81%

[a]Conversion determined by analysis of 400 MHz ^{1}H NMR of unpurified reaction mixture. [b]Enantioselectivity determined by GLC analysis (CDGTA) in comparison with authentic racemic material; the major isomer obtained with the *S*-biphen catalyst is the enantiomer of the isomer obtained with the *R*-TRIP catalysts.

the desired product in 84% yield with 81% ee (Table 1.7).[51] Compared with other catalysts screened, including Mo(N-2,6-i-$Pr_2C_6H_3$)(CHCMe$_2$Ph)(*S*-biphen) and Mo(N-2,6-i-$Pr_2C_6H_3$)(CHCMe$_2$Ph)(*R*-TRIP)(THF), catalyst **19** gave the highest % ee of the spirocyclic product. Mo(N-2,6-i-$Pr_2C_6H_3$)(CHCMe$_2$Ph)(*S*-biphen) led to complete conversion to the spirocycle, however the product was only 51% ee. There are few other known asymmetric syntheses of tertiary ethers[61,62] which highlights the synthetic efficiency of ARCM in giving products that are difficult to produce by known synthetic methods.

Table 1.8. Desymmetrization of triene acetals to give cyclic acetal, 26.



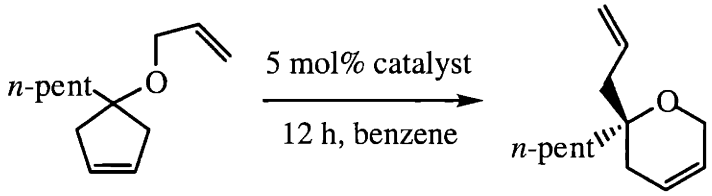
26

catalyst	Conv[a]	% ee[b] R = H
Mo(N-2,6-i-$Pr_2C_6H_3$)(CHCMe$_2$Ph)(*S*-biphen)	100%	22%
Mo(N-2,6-i-$Pr_2C_6H_3$)(CHCMe$_2$Ph)(*S*-TRIP)(THF)	100%	62%
Mo(N-2,6-$Cl_2C_6H_3$)(CHCMe$_3$)(*S*-biphen)(THF), **16**	100%	82%
		R = Me
Mo(N-2,6-i-$Pr_2C_6H_3$)(CHCMe$_2$Ph)(*S*-biphen)	100%	29%
Mo(N-2,6-i-$Pr_2C_6H_3$)(CHCMe$_2$Ph)(*S*-TRIP)(THF)	100%	51%
Mo(N-2,6-$Cl_2C_6H_3$)(CHCMe$_3$)(*S*-biphen)(THF), **16**	100%	83%

[a]Conversion determined by analysis of 400 MHz ^{1}H NMR of unpurified reaction mixture. [b]Enantioselectivity determined by GLC analysis (α-DEX) in comparison with authentic racemic material.

In the desymmetrization of triene acetals, Mo(N-2,6-$Cl_2C_6H_3$)(CHCMe$_3$)(*S*-biphen)(THF), **16**, gave the unsaturated cyclic acetal product, **26**, in ~82% ee from two different substrates (Table 1.8).[52] The enantioselectivity of catalyst **16** far surpassed Mo(N-2,6-i-$Pr_2C_6H_3$)(CHCMe$_2$Ph)(*S*-biphen) and Mo(N-2,6-i-$Pr_2C_6H_3$)(CHCMe$_2$Ph)(*R*-TRIP)(THF) in both reactions. In the asymmetric ring-opening/ring-closing reaction to give the cyclic tertiary ether, **27**, catalysts Mo(N-2,6-$Cl_2C_6H_3$)(CHCMe$_3$)(*R*-TRIP)(THF), **19**, and Mo(N-2,6-i-$Pr_2C_6H_3$)(CHCMe$_2$Ph)(*R*-TRIP)(THF) gave the highest enantioselectivities of all catalysts screened in the reaction (Table 1.9).[50] The conversion to ring-closed product for catalyst **19** was

Table 1.9. Enantioselective synthesis of heterocycle 27.

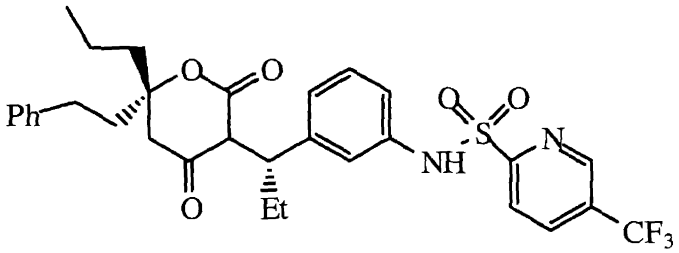


27

catalyst	Conv[a]	% ee[b]
Mo(N-2,6-i-$Pr_2C_6H_3$)(CHCMe$_2$Ph)(*S*-biphen)	86%	15%
Mo(N-2,6-i-$Pr_2C_6H_3$)(CHCMe$_2$Ph)(*R*-TRIP)(THF)	91%	68%
Mo(N-2,6-$Cl_2C_6H_3$)(CHCMe$_3$)(*R*-TRIP)(THF), **19**	77%	66%

[a]Conversion determined by analysis of 400 MHz ^{1}H NMR of unpurified reaction mixture. [b]Enantioselectivity determined by chiral GLC analysis (CDGTA) in comparison with authentic racemic material; the major isomer obtained with the *S*-biphen catalyst is the enantiomer of the isomer obtained with the *R*-TRIP catalysts.

not as high as for Mo(N-2,6-i-$Pr_2C_6H_3$)(CHCMe$_2$Ph)(*R*-TRIP)(THF) (77% compared with 91% conversion), however the enantioselectivity of **19** in this reaction was high. Heterocycles such as **27** are among those being synthesized as models towards the total synthesis of the molecule tipranavir, **28**, which is currently in development as an anti-HIV (human immunodeficiency virus) pharmaceutical product.[63]



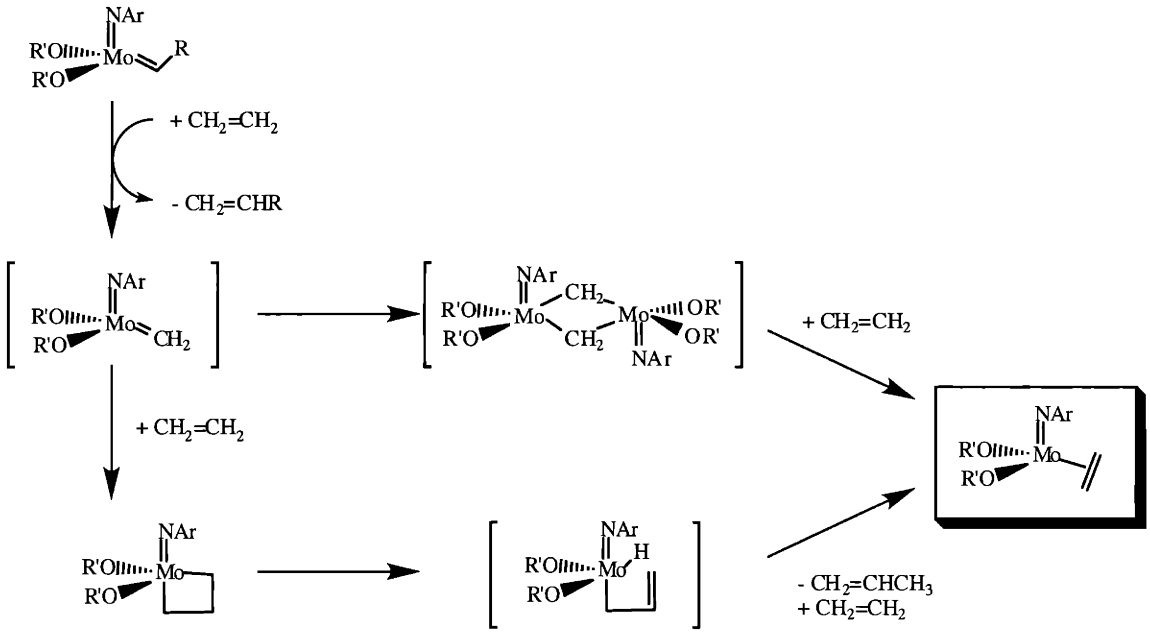
Tipranavir, **28**

1.5. Reaction of Mo(N-2,6-$Cl_2C_6H_3$)(CHCMe$_3$)(±-biphen)(THF) and Ethylene

In order to better elucidate the modes of ARCM catalyst decomposition, a current focus of research in our group is the reaction of ethylene with molybdenum imido alkylidene bisaryloxide complexes. W.-C. Peter Tsang showed that ethylene reacts with complexes containing chiral binaphtholate ligands to give relatively stable molybdacyclobutane products that can be observed in NMR studies.[46] For example, Mo(N-2,6-i-$Pr_2C_6H_3$)(CHCMe$_2$Ph)(*R*-TRIP)(THF) reacted with ethylene to give the molybdacyclobutane product, Mo(N-2,6-i-$Pr_2C_6H_3$)($CH_2CH_2CH_2$)(*R*-TRIP), which then decomposed over several days to give unidentified inorganic products and less than 1 equiv of propylene.

Molybdenum imido alkylidene bisalkoxide complexes have been shown to decompose to give olefin adducts. For example, Mo(N-2,6-i-$Pr_2C_6H_3$)(CHCMe$_3$)[OCMe(CF_3)$_2$]$_2$ reacted with an excess of vinyltrimethylsilane to give the olefin adduct, Mo(N-2,6-i-$Pr_2C_6H_3$)[OCMe(CF_3)$_2$]$_2$(η^2-CH_2=CHSiMe$_3$).[16,64] However, this complex was only characterized by NMR methods because it was thermally unstable in the solid state. An ethylene

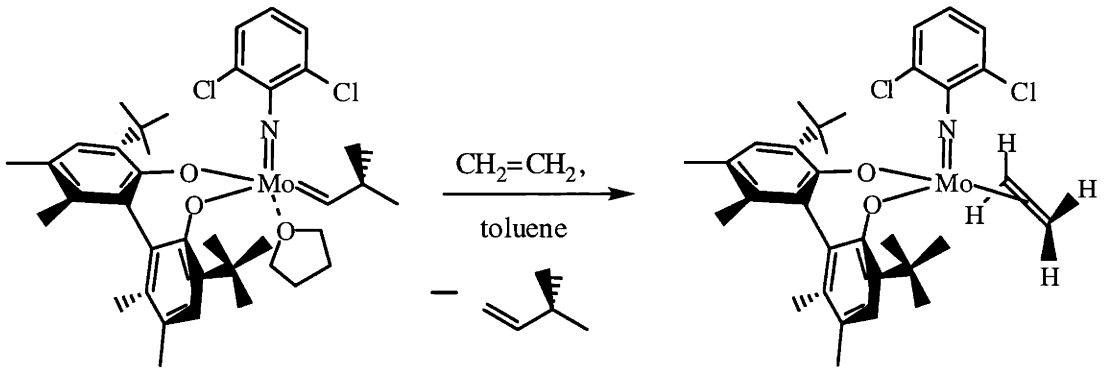
adduct is also the product of reaction between Mo(N-2,6-i-$Pr_2C_6H_3$)(CHCMe$_2$Ph)(*S*-biphen) and ethylene, however Mo(N-2,6-i-$Pr_2C_6H_3$)(*S*-biphen)(η^2-CH_2=CH_2) was only characterized by NMR studies and could not be isolated.[65] The postulated mechanisms of olefin adduct formation are bimolecular decomposition of the highly reactive molybdenum methylene complex or rearrangement of the molybdacyclobutane intermediate to eliminate propylene (Scheme 1.5).[5]



Scheme 1.5. Decomposition of Mo alkylidene complexes in the presence of ethylene.

Reaction of Mo(N-2,6-$Cl_2C_6H_3$)(CHCMe$_3$)(±-biphen)(THF), **16rac**, and ethylene, gave Mo(N-2,6-$Cl_2C_6H_3$)(±-biphen)(η^2-CH_2=CH_2), **29**, the first stable, isolated molybdenum imido bisaryloxide olefin complex. Compared with the decomposition products of other complexes, **29** shows remarkable stability and it is isolated as a bright orange powder in 94% yield (eq 7). The complex does not lose ethylene when dried *in vacuo*. If **29** is crystallized from ether, the complex coordinates one equiv ether, as confirmed in the X-ray crystal structure of the complex obtained by Sarah L. Aeilts and W.-C. Peter Tsang.

By ^{1}H NMR (500 MHz, C_6D_6) (Figure 1.8), the resonances for the ethylene protons appeared as three multiplets at 3.87, 3.53 and 3.06 in a 1:1:2 ratio. Resonances for the ethylene



16rac **29** (7)

carbon atoms appeared at 60.77 and 63.70 in the ^{13}C NMR (125 MHz, CD_2Cl_2) spectrum obtained by W.-C. Peter Tsang. Studies of **29**, including multidimensional NMR studies and reaction with $^{13}CH_2=^{13}CH_2$ to identify byproducts are currently underway (W.-C. Peter Tsang).

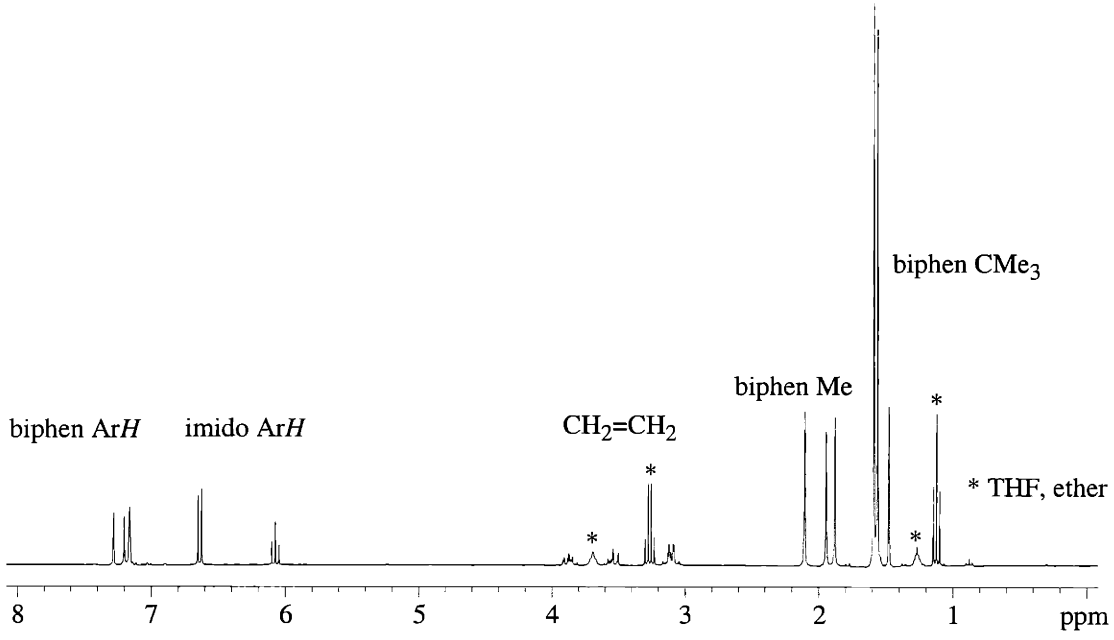


Figure 1.8. ^{1}H NMR spectrum (500 MHz, C_6D_6) of Mo(N-2,6-$Cl_2C_6H_3$)(±-biphen)(η^2-$CH_2=CH_2$), 29.

In addition, the reactivity of this complex is being investigated, with a focus on regenerating an alkylidene complex from **29**. All ARCM catalysts synthesized by our group thus far, including polymer-supported complexes,[48] decompose over time in the presence of olefins. Regenerating the reactive alkylidene would extend the lifetime of catalysts, allowing these to be recycled and reused.

CONCLUSIONS

In trying to expand the variety of imido ligands available for catalyst synthesis, the primary focus was to employ halogenated imido groups. Of all halogenated imido ligands studied, only the 2,6-dibromo-4-methylarylimido and 2,6-dichloroarylimido groups allowed for the synthesis and isolation of molybdenum imido alkylidene bisaryloxide complexes. In standard desymmetrization reactions, these complexes were found to be excellent ARCM catalysts, giving complete conversion to ring-closed product in less than an hour with high enantioselectivities in most cases. Complexes containing the 2,6-dichloroarylimido ligand have also given promising results in ARCM reactions performed by collaborators at Boston College. We cannot yet explain conclusively why the dichloroarylimido complexes show success in cases where other catalysts do not. Finally, reaction of Mo(N-2,6-$Cl_2C_6H_3$)($CHCMe_3$)(±-biphen) with ethylene gave the first stable, isolated decomposition product, Mo(N-2,6-$Cl_2C_6H_3$)(±-biphen)(η^2-CH_2=CH_2).

EXPERIMENTAL

General Details. All experiments were conducted under nitrogen in a Vacuum Atmospheres drybox or using standard Schlenk techniques. THF, ether, toluene, $Me_3SiOSiMe_3$ and pentane were sparged with nitrogen and passed through alumina. Benzene and dme were distilled from sodium benzophenone ketyl. Anhydrous Et_3N, $ClMgCH_2CMe_2Ph$, HOTf, $ClSiMe_3$, 1,4-dioxane, 2-$IC_6H_4NH_2$, 2,6-$Cl_2C_6H_3NH_2$, 2,6-Br_2-4-$CH_3C_6H_2NH_2$ and 2,4,6-$Cl_3C_6H_2NH_2$ were used as received from Aldrich. Na_2MoO_4, KH,(Strem) and 2,4,6-$F_3C_6H_2NH_2$ (Fluorochem)

were used as received. Benzyl potassium,[66] [*R*-TRIP]H_2,[43] [±-biphen]H_2,[40] [*S*-biphen]H_2,[42] [*S*-biad]H_2,[42] [*R*-benzhydril]H_2,[47] [*R*-mesbitet]K_2,[47] 3-(2,4-dimethylpentadienyl)allyl ether (**21**),[41] (3,5-dimethyl-(2*E*,5*E*)-heptadienyl)allyl ether (**22**),[41] and $ClMgCH_2CMe_3$[67] are synthesized by known procedures. [±-Biphen]H_2, [*S*-biphen]H_2, 3-(2,4-dimethylpentadienyl)allyl ether (**21**) and (3,5-dimethyl-(2*E*,5*E*)-heptadienyl)allyl ether (**22**) were gifts from John B. Alexander, [*S*-biad]H_2 was a gift from Jeffrey H. Houser, [*R*-benzhydril]H_2 was a gift from Stephen A. Miller, and [*R*-mesbitet]K_2 was a gift from Sarah J. Dolman. C_6D_6, CD_2Cl_2, THF-d_8 and toluene-d_8 were sparged with nitrogen and stored over 4Å molecular sieves. ^1H and ^{13}C NMR data are listed in parts per million downfield from tetramethylsilane and were referenced using the residual protonated solvent resonance. Routine coupling constants are not reported. ^{19}F NMR data was referenced externally using C_6F_6 in $CHCl_3$ as a standard (–164 ppm). Elemental analyses were performed by H. Kolbe Laboratories, Mülheim an der Ruhr, Germany.

Mo(N-2-IC_6H_4)$_2Cl_2$(dme) (1)

Na_2MoO_4 (3.90 g, 18.95 mmol), Et_3N (7.67 g, 75.79 mmol), $ClSiMe_3$ (21.6 mL, 171 mmol), 2-$IC_6H_4NH_2$ (8.30 g, 37.89 mmol) and dme (150 mL) were mixed in a Teflon-sealed flask and heated to 80 °C for 22h. The dark red mixture was filtered through Celite, leaving behind insoluble black crystals. The dme was evaporated giving the product as a dark red solid (6.64 g, 50.7%). ^1H NMR (500 MHz, C_6D_6): 7.66 (d, 2, Ar*H*), 7.44 (d, 2, Ar*H*), 6.70 (t, 2, Ar*H*), 6.16 (t, 2, Ar*H*), 3.59 (br s, 6, OCH_3), 3.19 (s, 4, OCH_2). ^{13}C NMR (125 MHz, C_6D_6): 158.71, 138.81, 129.09, 128.69, 128.32, 127.91, 71.51, 64.23. Anal. Calcd. for $MoC_{16}H_{18}N_2Cl_2I_2O_2$: C 27.81, H 2.63, N 4.05, Cl 10.26; Found: C 27.94, H 2.73, N 4.08, Cl 10.18.

Mo(N-2-IC_6H_4)$_2$(CH_2CMe_3)$_2$ (2)

$ClMgCH_2CMe_3$ (1.58 M in ether, 6.05 mL, 9.55 mmol) was added to a solution of **1** (3.00 g, 4.34 mmol) in ether (70 mL) and stirred at room temperature for 18h. The mixture was then filtered through Celite and the ether evaporated to give the product as a dark red solid that was

recrystallized from a mixture of ether and pentane (2.74 g, 93.8%). ^{1}H NMR (500 MHz, C_6D_6): 7.60 (d, 2, Ar*H*), 7.23 (d, 2, Ar*H*), 6.77 (t, 2, Ar*H*), 6.29 (t, 2, Ar*H*), 2.40 (s, 4, C*H*$_2$), 1.23 (s, 18, C*H*$_3$). ^{13}C NMR (125 MHz, C_6D_6): 158.24, 139.31, 129.21, 128.68, 126.79, 126.42, 86.68, 36.03, 34.15.

Mo(N-2,4,6-$F_3C_6H_2$)$_2$$Cl_2$(dme) (3)

Na_2MoO_4 (15.17 g, 73.69 mmol), Et_3N (29.82 g, 294.7 mmol), $ClSiMe_3$ (85.0 mL, 663 mmol) and 2,4,6-$F_3C_6H_2NH_2$ (21.68 g, 147.4 mmol) were suspended in dme (400 mL) in a 1 L Teflon-sealed flask and heated to 60 °C for 40h. The red mixture was then filtered through Celite and the dme evaporated to give **3** as a dark red powder (37.19 g, 92.2%). ^{1}H NMR (500 MHz, C_6D_6): 6.02 (d, 2, Ar*H*), 6.00 (d, 2, Ar*H*), 3.67 (br s, 6, OC*H*$_3$), 3.23 (br s, 4, OC*H*$_2$). ^{13}C NMR (125 MHz, C_6D_6): 100.91, 100.69 (2 C), 100.48, 71.45, 64.12. ^{19}F NMR (282 MHz, C_6D_6): -107.63 (s), -115.39 (s). Anal. Calcd. for $MoC_{16}H_{14}N_2Cl_2F_6O_2$: C 35.12, H 2.58, N 5.12, Cl 12.96; Found: C 34.98, H 2.66, N 5.08, Cl 12.90.

Mo(N-2,4,6-$Cl_3C_6H_2$)$_2$$Cl_2$(dme) (4)

Na_2MoO_4 (3.19 g, 15.5 mmol), $ClSiMe_3$ (17.7 mL, 139 mmol), Et_3N (6.27 g, 61.9 mmol) and 2,4,6-$Cl_3C_6H_2NH_2$ (6.08 g, 31.0 mmol) were combined in dme (300 mL) in a Teflon-sealed 1L flask and heated to 70 °C for 44h., The reaction mixture was filtered through Celite and the dme evaporated to give a purple-red solid that was rinsed with ether to remove aniline impurities, leaving **4** as a purple-red solid (9.37 g, 87.2%). ^{1}H NMR (500 MHz, C_6D_6): 6.78 (s, 4, Ar*H*), 3.60 (br s, 6, OC*H*$_3$), 3.25 (br s, 4, OC*H*$_2$). ^{13}C NMR (125 MHz, C_6D_6): 151.03, 132.64, 132.37, 128.65, 71.86, 64.28. Anal. Calcd. for $MoC_{16}H_{14}N_2Cl_8O_2$: C 29.75, H 2.18, N 4.34, Cl 43.91; Found: C 29.89, H 2.22, N 4.39, Cl 43.82.

Mo(N-2,4,6-$Cl_3C_6H_2$)$_2$(CH_2CMe_2Ph)$_2$ (5)

$ClMgCH_2CMe_2Ph$ (0.58 M in ether, 5.90 mL, 3.42 mmol) was added dropwise to a suspension

of **4** (1.01 g, 1.56 mmol) in ether (30 mL) and stirred for 12h. The mixture was then filtered through Celite and the pad washed with THF to dissolve ether-insoluble orange product. 1,4-Dioxane (30 mL) was added to precipitate magnesium salts. The entire mixture was refiltered through Celite and the solvent evaporated to give a dark brown oil. The oil was dissolved in pentane and stored at –30 °C overnight to give the product as an orange powder (902 mg, 77.1%). ^{1}H NMR (500 MHz, C_6D_6): 7.38 (d, 4, Ar*H*), 7.15 (t, 4, Ar*H*), 7.02 (t, 2, Ar*H*), 6.88 (s, 4, Ar*H*), 2.04 (s, 4, CH_2), 1.44 (s, 12, CH_3). ^{13}C NMR (125 MHz, C_6D_6): 150.44, 150.18, 130.96, 130.00, 129.13, 128.30, 126.85, 126.79, 85.30, 40.76, 32.49.

Mo(N-2,4,6-$Cl_3C_6H_2$)$_2$(CH_2CMe_3)$_2$ (6)

Neopentylmagnesium chloride (0.47 M in ether, 7.32 mL, 3.44 mmol) was added over 10 min to a suspension of Mo(N-2,4,6-$Cl_3C_6H_2$)$_2$$Cl_2$(dme) (1.01 g, 1.56 mmol) in ether (30 mL) and stirred for 23h. The mixture was then filtered through Celite and the solvent evaporated to give a red oil. The oil was suspended in pentane and stored at –30 °C overnight to give a red oily solid. ^{1}H NMR (500 MHz, C_6D_6): 6.87 (s, 4, Ar*H*), 2.47 (s, 4, CH_2), 1.18 (s, 18, CH_3). ^{13}C NMR (125 MHz, C_6D_6): 150.48, 131.02, 130.28, 128.65, 88.51, 35.43, 33.62.

Mo(N-2,6-Br_2-4-$CH_3C_6H_2$)$_2$$Cl_2$(dme) (7)

Na_2MoO_4 (3.89 g, 18.87 mmol), $ClSiMe_3$ (22 mL, 170 mmol), Et_3N (7.64 g, 75.49 mmol) and 2,6-dibromo-4-methylaniline (10.00 g, 37.74 mmol) were combined in dme (200 mL) in a 1 L Teflon-sealed Schlenk flask and heated to 60 °C for 24h. The mixture was then filtered through Celite and the solids were washed with dme until the filtrate was clear. The solution was concentrated to give a precipitate that was isolated by filtration (7.50 g). Further product was isolated in additional crops, to give the desired product Mo(N-2,6-Br_2-4-$CH_3C_6H_2$)$_2$$Cl_2$(dme) as a dark red solid (10.90 g total, 73.8%). ^{1}H NMR (500 MHz, C_6D_6): 6.93 (s, 4, Ar*H*), 3.72 (s, 6, OCH_3), 3.28 (s, 4, OCH_2), 1.59 (s, 6, ArCH_3). ^{13}C NMR (125 MHz, C_6D_6): 153.01, 139.10,

133.28, 121.14, 71.46, 64.02, 20.39. Anal. Calcd. for $MoC_{18}H_{20}Br_4Cl_2N_2O_2$: C 27.62, H 2.58, N 3.58, Cl 9.06; Found: C 27.74, H 2.65, N 3.63, Cl 9.14.

Mo(N-2,6-Br_2-4-$CH_3C_6H_2$)$_2$(CH_2CMe_3)$_2$ (8)

Mo(N-2,6-Br_2-4-$CH_3C_6H_2$)$_2Cl_2$(dme) (9.47 g, 12.09 mmol) was suspended in ether (100 mL) and $ClMgCH_2CMe_3$ (3.40 M in ether, 7.80 mL, 26.60 mmol) was added dropwise. The mixture was stirred for 15h and then filtered through Celite. The solvent was evaporated from the filtrate to give the product Mo(N-2,6-Br_2-4-$CH_3C_6H_2$)$_2$(CH_2CMe_3)$_2$ as dark red crystals (9.23 g, 100%). ^{1}H NMR (500 MHz, C_6D_6): 6.98 (s, 4, Ar*H*), 2.62 (s, 4, MoCH_2), 1.61 (s, 6, ArCH_3), 1.32 (s, 18, C(CH_3)$_3$). ^{13}C NMR (125 MHz, C_6D_6): 152.16, 136.94, 132.81, 120.49, 87.96, 34.89, 33.91, 20.39. Anal. Calcd. for $MoC_{24}H_{32}N_2Br_4$: C 37.73, H 4.22, N 3.67; Found: C 37.86, H 4.20, N 3.63.

Mo(N-2,6-Br_2-4-$CH_3C_6H_2$)(CHCMe_3)(OTf)$_2$(dme) (9)

HOTf (5.034 g, 33.54 mmol) was added to a −30 °C solution of Mo(N-2,6-Br_2-4-$CH_3C_6H_2$)$_2$(CH_2CMe_3)$_2$ (8.54 g, 11.18 mmol) in dme (50 mL) and the reaction was stirred for 12h. The solvent was evaporated to give an oily dark foam that was suspended in toluene, filtered through Celite and dried *in vacuo*. The resulting brown-yellow foam was triturated with ether and a yellow precipitate formed. The yellow powder was isolated by filtration to give the product Mo(N-2,6-Br_2-4-$CH_3C_6H_2$)(CHCMe_3)(OTf)$_2$(dme) in several crops (7.80 g total, 85.4%). ^{1}H NMR (500 MHz, C_6D_6) (~1:3 mixture of *anti*:*syn*): 14.96 (s, 1, Mo=C*H anti*, J_{CH} = 140 Hz), 14.13 (s, 1, Mo=C*H syn*, J_{CH} = 120 Hz), 6.75 (s, 2, Ar*H*), 3.87 (br s, 3, OCH_3), 3.67 (s, 2, OCH_2), 3.26 (s, 2, OCH_2), 2.91 (br s, 3, OCH_3), 1.54 (s, 9, C(CH_3)$_3$ *syn*), 1.49 (s, 9, C(CH_3)$_3$ *anti*), 1.31 (s, 3, ArCH_3). ^{13}C NMR (125 MHz, C_6D_6): (mixture of *anti* and *syn*) 331.50, 151.24, 142,44, 142.06, 133.81, 123.80, 121.74, 119.21, 77.56, 73.57, 70.44, 70.23, 66.26, 62.33, 61.33, 53.29, 30.81, 30.47, 20.68. ^{19}F NMR: (282 MHz, C_6D_6): −77.95 (s). Anal. Calcd. for $MoC_{18}H_{25}NO_8Br_2F_6S_2$: C 26.45, H 3.08, N 1.71; Found: C 26.62, H 3.01, N 1.75.

Mo(N-2,6-Br_2-4-$CH_3C_6H_2$)(CHCMe$_3$)(*R*-benzhydril)(THF) (10)

A suspension of potassium hydride (38 mg, 0.94 mmol) in THF (2 mL) was added to [*R*-benzhydril]H_2 (268 mg, 0.43 mmol) in THF (2 mL) and stirred for 2h until no further gas evolution was observed. The solution was then added to Mo(N-2,6-Br_2-4-$CH_3C_6H_2$)(CHCMe$_3$)(OTf)$_2$(dme) (350 mg, 0.43 mmol) in THF (4 mL) and stirred for 18h. The solvent was evaporated and the residue dissolved in minimal ether and pentane to give the product, Mo(N-2,6-Br_2-4-$CH_3C_6H_2$)(CHCMe$_3$)(*R*-benzhydril)(THF), as a golden yellow powder (107 mg, 22.2%). ^{1}H NMR (500 MHz, C_6D_6) (~1:4 mixture of *anti*:*syn*): 14.51 (s, 1, Mo=C*H* *anti*), 12.81 (s, 1, Mo=C*H* *syn*, J_{CH} = 123 Hz), 7.53 (d, 2, Ar*H*), 7.49 (d, 2, Ar*H*), 7.34 (d, 2, Ar*H*), 7.23 (t, 3 Ar*H*), 7.19-7.14 (m, 5, Ar*H*), 7.11-7.06 (m, 4, Ar*H*), 7.02 (s, 2, Ar*H*), 6.94-6.90 (m, 3, Ar*H*), 6.78 (s, 1, Ar*H*), 6.33 (br s, 1, C*H*Ph$_2$), 6.13 (br s, 1, C*H*Ph$_2$), 3.71-3.68 (m, 4, THF), 2.82-2.31 (m, 8, ArC*H*$_2$), 1.68 (s, 3, ArC*H*$_3$), 1.57-1.42 (br m, 8 ArCH$_2$C*H*$_2$), 1.25 (s, 9, C(C*H*$_3$)$_3$), 1.20 (m, 4, THF). ^{13}C NMR (125 MHz, C_6D_6): 311.18, 159.47, 152.22, 146.74, 146.46, 145.87, 145.76, 137.22, 136.18, 134.92, 132.83, 130.88, 130.85, 130.30, 129.94, 129.03, 128.86, 127.23, 126.97, 126.53, 126.31, 125.97, 72.61, 52.21, 51.06, 48.28, 32.76, 30.44, 30.41, 29.06, 28.90, 25.80, 24.43, 24.27, 23.85, 23.79, 20.32. Anal. Calcd. for $MoC_{62}H_{63}NO_3Br_2$: C 66.14, H 5.64, N 1.24; Found: C 66.03, H 5.71, N 1.27.

Mo(N-2,6-$Cl_2C_6H_3$)$_2$$Cl_2$(dme) (11)

Na_2MoO_4 (20.00 g, 97.13 mmol), Me_3SiCl (148 mL, 1170 mmol), Et_3N (39.32 g, 388.5 mmol), 2,6-$Cl_2C_6H_3NH_2$ (31.47 g, 194.3 mmol) and dme (500 mL) were mixed in a 1L flask and the mixture was heated to 65 °C for 4 days to give a red suspension. Volatiles were then evaporated leaving a pink solid that was extracted with a Soxhlet apparatus using dme as a solvent. The dme was removed and the resulting red solid was dried *in vacuo* to yield Mo(N-2,6-$Cl_2C_6H_3$)$_2$$Cl_2$(dme) as a red solid (52.56 g, 93.8%). If necessary, the product can be recrystallized from ether to remove trace impurities seen by ^{1}H NMR. ^{1}H NMR (500 MHz,

C_6D_6): 6.79 (d, 4, Ar*H*), 6.11 (t, 2, Ar*H*), 3.61 (br s, 4, OCH_2), 3.21 (br s, 6, OCH_3). ^{13}C NMR (125 MHz, C_6D_6): 152.44, 132.38, 127.87, 118.40, 30.56, 23.07. Anal. Calcd. for $MoC_{16}H_{16}Cl_6N_2O_2$: C 33.31, H 2.80, N 4.86, Cl 36.87; Found: C 33.18, H 2.88, N 4.90, Cl 36.78.

Mo(N-2,6-$Cl_2C_6H_3$)$_2$(CH_2CMe_3)$_2$ (12)

Mo(N-2,6-$Cl_2C_6H_3$)$_2Cl_2$(dme) (15.82 g, 27.42 mmol) was dissolved in ether (150 mL) and $ClMgCH_2CMe_3$ (1.46 M in ether, 42.0 mL, 60.3 mmol) was added dropwise. The mixture was stirred for 18 h, filtered through Celite and evaporated to give the product as a red powder that was recrystallized from pentane (15.20 g, 99.3%). ^{1}H NMR (500 MHz, C_6D_6): 6.88 (d, 4, Ar*H*), 6.21 (t, 2, Ar*H*), 2.55 (s, 4, CH_2), 1.23 (s, 18, CH_3). ^{13}C NMR (125 MHz, C_6D_6): 151.81, 130.79, 128.37, 125.56, 87.69, 35.30, 33.73. Anal. Calcd. for $MoC_{22}H_{28}Cl_4N_2$: C 47.34, H 5.06, N 5.02, Cl 25.40; Found: C 47.30, H 5.11, N 5.00, Cl 25.27.

Mo(N-2,6-$Cl_2C_6H_3$)$_2$(CH_2CMe_2Ph)$_2$ (13)

$ClMgCH_2CMe_2Ph$ (0.62 M in ether, 31.0 mL, 19.1 mmol) was added dropwise to a solution of Mo(N-2,6-$Cl_2C_6H_3$)$_2Cl_2$(dme) (5.00 g, 8.67 mmol) in ether (100 mL). After stirring for 19h, the mixture was filtered through Celite and the ether evaporated to give Mo(N-2,6-$Cl_2C_6H_3$)$_2$(CH_2CMe_2Ph)$_2$ as a brown-orange solid (5.91 g, 100%). ^{1}H NMR (500 MHz, C_6D_6): 7.41 (d, 4, Ar*H*), 7.16 (t, 4, Ar*H*), 7.01 (t, 2, Ar*H*), 6.85 (d, 2, Ar*H*), 6.19 (t, 2, Ar*H*), 2.10 (s, 4, MoCH_2), 1.47 (s, 12, CH_3). ^{13}C NMR (125 MHz, C_6D_6): 150.51, 130.73, 129.09, 128.26, 126.95, 126.66, 125.37, 84.73, 40.66, 32.50. Anal. Calcd. for $MoC_{32}H_{32}Cl_4N_2$: C 56.33, H 4.73, N 4.11, 20.78; Found: C 56.46, H 4.72, N 3.75, Cl 20.78.

Mo(N-2,6-$Cl_2C_6H_3$)($CHCMe_3$)(OTf)$_2$(dme) (14)

Pure and dry starting materials and solvents are imperative to the success of this procedure.

Purification requires *complete* evaporation of solvent. If an oil or gummy solid is obtained from the various extractions further removal of solvent is *required* (lyophilization with benzene is suggested) in order to obtain pure materials in good yield. Into a 500 mL flask was placed a solution of Mo(N-2,6-$Cl_2C_6H_3$)$_2$(CH_2CMe_3)$_2$ (13.52 g, 24.22 mmol) in dme (150 mL). This solution was cooled to –30 °C and HOTf (10.90 g, 72.65 mmol) was added dropwise to yield a dark brown solution that was stirred for 18 h. The solvent was then evaporated to give a brown foam that was dissolved in toluene and filtered through Celite. Toluene was evaporated, leaving a brown solid that was dissolved in a mixture of ether and pentane and stored at –30 °C to give a brown powder. The brown powder was isolated by filtration and washed with cold ether to give Mo(N-2,6-$Cl_2C_6H_3$)(CHCMe$_3$)(OTf)$_2$(dme) as a yellow solid (9.64 g, 55.7%). ^{1}H NMR (500 MHz, C_6D_6): (1:4 mixture *anti*: *syn*) 14.98 (s, 1, Mo=C*H anti*), 14.08 (s, 1, Mo=C*H syn*, J_{CH} = 121 Hz), 6.59 (d, 2, Ar*H*), 6.15 (t, 1, Ar*H* dme), 3.80 (br s, 4, OCH_2), 2.82 (br s, 6, OCH_3), 1.47 (s, 9, C(CH_3)$_3$). ^{13}C NMR (125 MHz, C_6D_6): (mix *syn*/*anti*) 340.57, 330.98, 150.33, 149.78, 135.81, 130.12, 129.10, 124.26, 121.86, 121.73, 119.33, 119.20, 116.66, 77.97, 73.88, 70.24, 66.18, 62.38, 61.26, 53.17, 30.63. ^{19}F NMR (282 MHz, C_6D_6): –78.94 (s). Anal. Calcd. for $MoC_{17}H_{23}NCl_2F_6S_2O_8$: C 28.58, H 3.25, N 1.96, Cl 9.93; Found: C 28.67, H 3.26, N 2.10, Cl 9.86.

Mo(N-2,6-$Cl_2C_6H_3$)(CHCMe$_2$Ph)(OTf)$_2$(THF)$_x$ (15)

HOTf (3.77 g, 25.15 mmol) was added to a –30 °C solution of Mo(N-2,6-$Cl_2C_6H_3$)$_2$(CH_2CMe_2Ph)$_2$ (5.72 g, 8.38 mmol) in dme (80 mL). After stirring for 16 h, the dme was evaporated and the resulting brown oil was dissolved in toluene and filtered through Celite. Evaporation of the toluene yielded a brown oily solid that was dissolved in ether and cooled to –30 °C. Upon warming, a brown yellow solid formed and was triturated with THF and ether several times to give the product as a yellow powder (1.75 g, 27.5%). In the solid state, the complex existed as a mono(THF) adduct while in THF, it existed as a 1:1 mixture of two bis(THF) adducts. ^{1}H NMR (500 MHz, THF-d_8): 14.21 (s, 1, Mo=C*H*, J_{CH} = 126 Hz), 14.17 (s,

1, Mo=C*H*, J_{CH} = 124 Hz), 6.96 (d, 4, Ar*H*), 6.92 (d, 2, Ar*H*), 6.87 (d, 2, Ar*H*), 6.78 (t, 1, Ar*H*), 6.71 (m, 3, Ar*H*), 6.55 (m, 3, Ar*H*), 6.30 (t, 1, Ar*H*), 3.69 (m, 4, THF), 3.54 (m, 4, THF), 3.44 (m, 4, THF), 2.82 (m, 4, THF), 1.21 (s, 3, CH_3), 1.20 (s, 6, CH_3), 0.94 (s, 3, CH_3). ^{13}C NMR (125 MHz, THF-d_8): 339.46, 151.02, 148.06, 147.41, 135.82, 131.2, 130.79, 130.25, 129.69, 129.13, 127.88, 127.73, 127.33, 122.23, 119.70, 83.68, 82.97, 68.37, 66.48, 59.22, 30.67, 30.31, 29.77, 27.07, 26.53, 15.84. ^{19}F NMR (282 MHz, THF-d_8): –80.14 (s), –80.52 (s), –81.10 (s), –81.33 (s). Anal. Calcd. for $MoC_{22}H_{23}Cl_2NO_7F_6S_2$: C 34.84, H 3.06, N 1.85, Cl 9.35; Found: C 34.68, H 2.93, N 1.81, Cl 9.39.

Mo(N-2,6-$Cl_2C_6H_3$)(CHCMe_3)(*S*-biphen)(THF) (16)

Benzyl potassium (182 mg, 1.40 mmol) in THF (1 mL) was added to [*S*-biphen]H_2 (248 mg, 0.70 mmol) in THF (1 mL) until a slight orange color persisted. This solution was then added to Mo(N-2,6-$Cl_2C_6H_3$)(CHCMe_3)(OTf)$_2$(dme) (500 mg, 0.70 mmol) in THF (2 mL), turning the mixture dark red. After stirring for 17 h, the solvent was evaporated and the resulting residue extracted with benzene and filtered through Celite. The benzene was evaporated and the resulting red foam was dissolved in a small amount of ether and stored at –30 °C to yield Mo(N-2,6-$Cl_2C_6H_3$)(CHCMe_3)(*S*-biphen)(THF) as ruby red crystals (287 mg, 54.6%). ^{1}H NMR (500 MHz, C_6D_6): 11.31 (s, 1, Mo=C*H*, J_{CH} = 120 Hz), 7.44 (s, 1, Ar*H*), 7.12 (s, 1, Ar*H*), 6.72 (d, 2, Ar*H*), 6.11 (t, 1, Ar*H*), 3.60 (br m, 4, THF), 2.14 (s, 3, ArCH_3), 2.07 (s, 3, ArCH_3), 1.73 (s, 3, ArCH_3), 1.71 (s, 3, ArCH_3), 1.60 (s, 18, ArC(CH_3)$_3$), 1.31 (br m, 4, THF), 1.12 (s, 9, Mo=CHC(CH_3)$_3$). ^{13}C NMR (125 MHz, C_6D_6): 298.34, 158.73, 157.83, 151.71, 138.60, 136.26, 135.77, 134.47, 132.03, 130.98, 130.42, 130.19, 129.84, 129.72, 129.58, 129.18, 126.27, 66.26, 48.64, 35.86, 35.77, 31.79, 31.46, 31.18, 30.49, 28.88, 25.78, 20.92, 20.78, 17.36, 17.10, 15.94. Anal. Calcd. for $MoC_{39}H_{53}Cl_2NO_3$: C 62.40, H 7.12, N 1.87, Cl 9.45; Found C 62.29, H 7.19, N 1.94, Cl 9.41.

Mo(N-2,6-$Cl_2C_6H_3$)(CHCMe_3)(*R*-benzhydril)(THF) (17)

KH (43 mg, 1.06 mmol) was added to [*R*-benzhydril]H_2 (303 mg, 0.48 mmol) in THF (8 mL). After stirring for 1.5h, the mixture was filtered through Celite and added to Mo(N-2,6-$Cl_2C_6H_3$)(CHCMe_3)(OTf)$_2$(dme) (345 mg, 0.48 mmol). After stirring for 16h, the red solution was evaporated to dryness and the resulting solid suspended in toluene and filtered through Celite to remove salt impurities. The toluene was evaporated and yellow solid precipitated as the volume was reduced. The solid was dried *in vacuo*, suspended in ether and filtered to isolate Mo(N-2,6-$Cl_2C_6H_3$)(CHCMe_3)(*R*-benzhydril)(THF), **19**, as a golden yellow powder (234 mg total, 46.8%). ^{1}H NMR (500 MHz, C_6D_6): 12.51 (s, 1, Mo=C*H*, J_{CH} = 121 Hz), 7.48 (d, 2, Ar*H*), 7.44 (d, 2, Ar*H*), 7.32 (d, 2, Ar*H*), 7.19 (t, 2, Ar*H*), 7.14 (d, 2, Ar*H*), 7.10 (s, 1, Ar*H*), 7.08-7.04 (m, 3, Ar*H*), 7.00-6.99 (m, 4, Ar*H*), 6.89 (br d, 2, Ar*H*), 6.76 (d, 2, Ar*H* *meta* imido), 6.75 (s, 1, Ar*H*), 6.37 (br s, 1, C*H*Ph$_2$), 6.26 (t, 1, Ar*H* *para* imido), 5.92 (br s, 1, C*H*Ph$_2$), 3.78 (br s, 2, THF), 3.61 (br s, 2, THF), 2.85-2.81 (m, 1, CH_2), 2.75-2.70 (m, 1, CH_2), 2.67-2.56 (m, 5, CH_2), 2.32-2.29 (m, 1, CH_2), 1.70-1.64 (m, 1, CH_2), 1.61-1.58 (m, 4, CH_2), 1.54-1.47 (m, 2, CH_2), 1.43-1.41 (m, 1, CH_2), 1.24 (s, 9, CH_3). ^{13}C NMR (125 MHz, C_6D_6): 311.82, 160.03, 151.22, 146.86, 146.64, 145.69, 136.17, 134.84, 133.01, 130.76, 130.68, 130.34, 129.81, 129.01, 128.83, 126.99, 126.52, 126.22, 125.95, 125.36, 74.34, 52.27, 50.86, 47.86, 32.53, 30.41, 30.35, 29.03, 28.87, 25.66, 24.39, 24.32, 23.77. Anal. Calcd. for $MoC_{62}H_{61}NO_3Cl_2$: C 71.95, H 5.94, N 1.35, Cl 6.85; Found: C 72.09, H 6.05, N 1.31, Cl 6.81.

Mo(N-2,6-$Cl_2C_6H_3$)(CHCMe_3)(*S*-biad) (18)

A THF solution (2 mL) of benzyl potassium (47 mg, 0.36 mmol) was added to a suspension of [*S*-biad]H_2 (92 mg, 0.18 mmol) in THF (2 mL) until a pale orange color persisted. This solution was then added to Mo(N-2,6-$Cl_2C_6H_3$)(CHCMe_3)(OTf)$_2$(dme) (128 mg, 0.18 mmol) in THF (1 mL). After stirring for 16h, the solvent was evaporated and the residue extracted with toluene and filtered through Celite. The toluene was evaporated and the residue redissolved in ether (1 mL) to give Mo(N-2,6-$Cl_2C_6H_3$)(CHCMe_3)(*S*-biad) as ruby red blocks (91 mg, 60.7%). ^{1}H

NMR (500 MHz, C_6D_6): 11.05 (s, 1, Mo=C*H*, J_{CH} = 122 Hz), 7.42 (s, 1, Ar*H* biphen), 7.12 (s, 1, Ar*H* biphen), 6.73 (d, 2, Ar*H* imido), 6.14 (t, 1, Ar*H* imido), 2.41 (m, 12, adamantyl CH_2), 2.25 (s, 3, ArCH_3), 2.21-2.15 (m, 6, adamantyl C*H*), 2.05 (s, 3, ArCH_3), 1.87 (m, 12, adamantyl-CH_2), 1.78 (s, 3, ArCH_3), 1.70 (s, 3, ArCH_3), 1.16 (s, 9, C(CH_3)$_3$). ^{13}C NMR (125 MHz, C_6D_6) 316.29, 156.14, 151.41, 140.63, 138.08, 135.99, 135.01, 134.54, 134.39, 133.37, 131.66, 130.42, 129.64, 127.20, 126.03, 121.72, 110.13, 48.43, 41.73, 41.20, 37.98, 37.89, 31.81, 30.11, 29.98, 20.97, 20.80, 20.54, 17.30, 16.94, 16.38. Anal. Calcd. for $MoC_{47}H_{57}Cl_2NO_2$: C 67.62, H 6.88, N 1.68, Cl 8.49; Found: C 67.55, H 6.94, N 1.63, Cl 8.57.

Mo(N-2,6-$Cl_2C_6H_3$)(CHCMe$_3$)(*R*-TRIP)(THF) (19)

A solution of benzyl potassium (340 mg, 2.60 mmol) in THF (5 mL) was added to [*R*-TRIP]H_2 (899 mg, 1.30 mmol) in THF (20 mL) until endpoint and then added to a –30 °C solution of Mo(N-2,6-$Cl_2C_6H_3$)(CHCMe$_3$)(OTf)$_2$(dme) (929 mg, 1.30 mmol) in THF (40 mL). After 20h, THF was evaporated and the residue suspended in toluene and filtered through Celite. The toluene was evaporated and the resulting residue was then dissolved in a minimal amount of ether. An equal volume of $Me_3SiOSiMe_3$ was added, with 2 drops of THF, and the solution was stored at –30 °C for 24h, to give a brownish yellow solid. The solid was filtered and rinsed with cold $Me_3SiOSiMe_3$ and ether to give Mo(N-2,6-$Cl_2C_6H_3$)(CHCMe$_3$)(*R*-TRIP)(THF) as a dark yellow solid (690 mg, 48.9%). ^{1}H NMR (500 MHz, C_6D_6): 13.24 (s, 1, Mo=C*H*, J_{CH} = 121 Hz), 7.96 (s, 1, Ar*H*), 7.74 (d, 1, Ar*H*), 7.72 (d, 1, Ar*H*), 7.46 (d, 1, Ar*H*), 7.31 (s, 1, Ar*H*), 7.26 (d, 1, Ar*H*), 7.16-7.07 (m, 6, Ar*H*), 6.98 (t, 1, Ar*H*), 6.78 (br m, 1, Ar*H*), 6.44 (br m, 1, Ar*H*), 6.05 (t, 1, Ar*H*), 3.39 (br sept, 1, C*H*Me$_2$), 3.30 (br sept, 1, C*H*Me$_2$), 3.18 (br m, 4, THF), 3.13 (br sept, 1, C*H*Me$_2$), 3.05 (sept, 1, C*H*Me$_2$), 2.94 (sept, 1, C*H*Me$_2$), 2.76 (sept, 1, C*H*Me$_2$), 1.42 (d, 3, CH(CH_3)$_2$), 1.38 (d, 3, CH(CH_3)$_2$), 1.36 (d, 3, CH(CH_3)$_2$), 1.31 (s, 9, Mo=CHCCH_3), 1.30 (d, 3, CH(CH_3)$_2$), 1.24 (d, 3, CH(CH_3)$_2$), 1.20 (m, 4, THF), 1.09 (d, 3, CH(CH_3)$_2$), 1.07 (d, 6, CH(CH_3)$_2$), 0.97 (br d, 6, CH(CH_3)$_2$). ^{13}C NMR (125 MHz, C_6D_6): 317.51, 165.75, 161.96, 151.33, 148.63, 148.53, 148.10, 147.82, 147.72, 146.98, 137.28, 136.04, 135.76, 135.52, 132.63,

132.50, 131.29, 130.42, 130.28, 130.20, 128.74, 128.67, 128.29, 127.97, 127.78, 126.27, 126.14, 126.03, 125.37, 123.69, 123.16, 121.19, 120.86, 120.77, 120.20, 119.92, 75.11, 48.44, 35.39, 35.03, 31.95, 31.26, 28.04, 26.76, 25.73, 25.65, 25.09, 24.97, 24.85, 24.77, 24.27, 24.08, 24.02. Anal. Calcd. for $MoC_{65}H_{77}NO_3Cl_2$: C 71.81, H 7.14, N 1.29, Cl 6.52; Found: C 71.65, H 7.20, N 1.19, Cl 6.53.

Mo(N-2,6-$Cl_2C_6H_3$)(CHCMe$_3$)(*R*-mesbitet)(THF) (20)

[*R*-mesbitet]K_2 (327 mg, 0.54 mmol) was added to Mo(N-2,6-$Cl_2C_6H_3$)(CHCMe$_3$)(OTf)$_2$(dme) (385 mg, 0.54 mmol) in THF (3 mL) and stirred for 17h. The solvent was evaporated to give a foam that was extracted with toluene, filtered through Celite and dried *in vacuo*. The resulting solid was dissolved in minimal ether and a drop of THF was added. After storing at –30 °C for several days, the product was isolated in several crops as orange-yellow gemstones (205 mg, 41.0%). ^{1}H NMR (500 MHz, C_6D_6): 12.89 (s, 1, Mo=C*H*, J_{CH} = 121 Hz), 7.01 (s, 1, Ar*H*), 7.00 (s, 1, Ar*H*), 6.97 (s, 1, Ar*H*), 6.82 (br s, 2, Ar*H*), 6.80 (s, 1, Ar*H*), 6.73 (br s, 2, Ar*H*), 6.19 (t, 1, Ar*H*), 3.10-3.05 (m, 2, CH_2), 3.05-3.00 (m, 2, CH_2), 2.97-2.90 (m, 1, CH_2), 2.86-2.78 (m, 6, CH_2), 2.68-2.62 (m, 1, CH_2), 2.64 (s, 3, ArCH_3), 2.56 (s, 3, ArCH_3), 2.56-2.50 (m, 1, CH_2), 2.35 (s, 6, ArCH_3), 2.13 (s, 3, ArCH_3), 1.82 (s, 3, ArCH_3), 1.82-1.79 (m, 1, CH_2), 1.74-1.66 (m, 3, CH_2), 1.66-1.60 (m, 2, CH_2), 1.49-1.42 (m, 1, CH_2), 1.18 (s, 9, C(CH_3)$_3$), 0.89 (br m, 4, THF). ^{13}C NMR (125 MHz, C_6D_6): 309.31, 159.97, 151.40, 138.92, 138.76, 138.52, 136.57, 136.45, 136.09, 135.92, 135.57, 135.39, 132.41, 130.70, 130.47, 129.09, 128.99, 128.76, 128.02, 125.01, 73.57, 47.50, 32.15, 30.41, 30.29, 29.28, 29.04, 25.40, 24.54, 24.40, 24.15, 24.02, 22.91, 21.81, 21.73, 21.61, 21.36, 21.24. Anal. Calcd. for $MoC_{53}H_{61}NO_3Cl_2$: C 68.68, H 6.63, N 1.51, Cl 7.65; Found: C 68.78, H 6.71, N 1.57, Cl 7.54.

Mo(N-2,6-$Cl_2C_6H_3$)(η^2-C_2H_4)(±-biphen) (29)

Mo(N-2,6-$Cl_2C_6H_3$)(CHCMe$_3$)(±-biphen)(THF) (167 mg, 0.22 mmol) was dissolved in toluene (4 mL) and put under an atmosphere of ethylene (1 atm) via three freeze-pump-thaw cycles. The

color changed to dark red and after stirring for 24h, the solvent was removed *in vacuo* to give Mo(N-2,6-$Cl_2C_6H_3$)(η^2-C_2H_4)(±-biphen) as an orange powder (133 mg, 93.9%). ^{1}H NMR (500 MHz, C_6D_6): 7.29 (s, 1, Ar*H*), 7.20 (s, 1, Ar*H*), 6.65 (d, 2, Ar*H* imido), 6.07 (t, 1, Ar*H* imido), 3.87 (m, 1, CH_2=CH_2), 3.53 (m, 1, CH_2=CH_2), 3.06 (m, 2, CH_2=CH_2), 2.12 (s, 3, ArCH_3), 2.02 (s, 3, ArCH_3), 1.90 (s, 3, ArCH_3), 1.57 (s, 9, C(CH_3)$_3$), 1.55 (s, 9, C(CH_3)$_3$), 1.50 (s, 3, ArCH_3). ^{13}C NMR (125 MHz, CD_2Cl_2): 162.66, 152.74, 149.58, 141.18, 137.16, 134.31, 133.75, 133.32, 132.10, 131.24, 129.27, 128.08, 127.69, 127.10, 126.48, 125.30, 72.19, 63.70, 60.77, 35.80, 34.54, 30.68, 30.23, 29.85, 26.11, 20.43, 20.15, 17.06, 16.48. Anal. Calcd. for $MoC_{32}H_{39}NO_2Cl_2$: C 60.38, H 6.18, N 2.20, Cl 11.14; Found: C 60.26, H 6.25, N 2.04, Cl 11.22.

Representative Procedure for Asymmetric Ring-Closing Metathesis Reactions

Mo(N-2,6-$Cl_2C_6H_3$)(CHCMe$_3$)(*S*-biphen)(THF), **16**, (5 mg) and C_6D_6 (0.50 mL added via syringe) were added to triene **22** (17 mg, 0.10 mmol) and stirred vigorously in a loosely capped scintillation vial. The reaction mixture was transferred to an NMR tube after ~45-60 min and the conversion determined by ^{1}H NMR (500 MHz). The volatile components were isolated by vacuum transfer and the product ee was determined by standard chiral GLC.

Chapter 2

SYNTHESIS OF MOLYBDENUM IMIDO ALKYLIDENE COMPLEXES CONTAINING N,N'-DISUBSTITUTED-2,2'-DIAMINO-1,1'-BINAPHTHYL LIGANDS

Material appearing in this chapter has also appeared in print:
J.Y. Jamieson, R.R. Schrock, W.M. Davis, P.J. Bonitatebus, S.S. Zhu, A.H. Hoveyda. "Synthesis and Study of Molybdenum Imido Alkylidene Complexes Containing N,N'-Disubstituted-2,2'-Diamino-1,1'-Binaphthyl Ligands" *Organometallics* **2000**, *19*, 925.

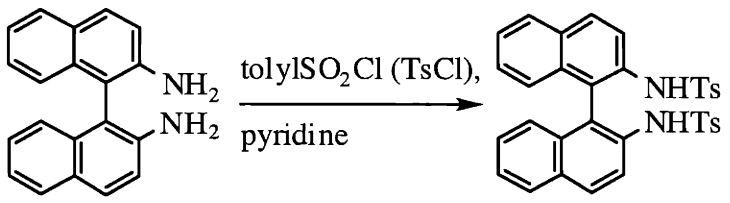
INTRODUCTION

The enantioselectivity of molybdenum imido alkylidene catalysts in asymmetric ring-closing metathesis (ARCM) is effectively controlled by optically pure bisaryloxide ligands. Examples of these optically pure bisaryloxide ligands include [*S*-biphen],[40,42] [*R*-TRIP],[43] and [*R*-bitet].[44] In seeking to expand the variety of chiral ligands useful for ARCM catalysis, the goal was to explore the reactivity of molybdenum imido alkylidene diamido complexes derived from 2,2'-diamino-1,1'-binaphthyl.[68,69] The only other diamido ligand that had been previously used to stabilize group 6 imido alkylidene complexes is the bis(trimethylsilyl)*o*-phenylenediamido ligand for both tungsten[70-72] and molybdenum.[73] For example, when the dialkyl complex $W(NPh)(CH_2CMe_3)_2[o\text{-}(Me_3SiN)_2C_6H_4]$ was heated to 70 °C in toluene with an excess of PMe_3, the alkylidene complex $W(NPh)(CHCMe_3)[o\text{-}(Me_3SiN)_2C_6H_4](PMe_3)$ was generated. This tungsten alkylidene complex catalyzes the ring-opening metathesis polymerization (ROMP) of norbornene only when PMe_3 dissociates from the metal.

RESULTS AND DISCUSSION

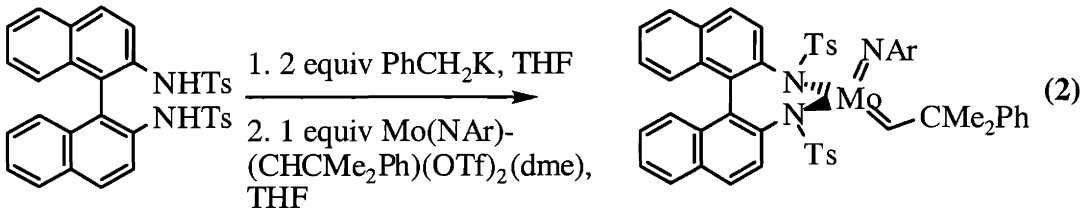
2.1. Synthesis and Characterization of Molybdenum Imido Alkylidene Complexes of $[BINA(NTs)_2]H_2$

The first diamine prepared was 2,2'-bis-*p*-tolylsulfonamido-1,1'-binaphthyl ($[BINA(NTs)_2]H_2$, **30**), synthesized by S. Sherry Zhu by reaction of 2,2'-diamino-1,1'-binaphthyl with *p*-toluenesulfonyl chloride in pyridine (eq 1). Addition of methanol to the solution caused the precipitation of the product as a white solid. Recrystallization from dichloromethane afforded **30** in essentially quantitative yield.



30 **(1)**

A series of molybdenum imido alkylidene complexes of **30** were then synthesized. Diamine **30** was deprotonated with benzyl potassium and added to Mo(N-2,6-i-$Pr_2C_6H_3$)(CHCMe$_2$Ph)(OTf)$_2$(dme). The product was isolated by standard procedures to give Mo(N-2,6-i-$Pr_2C_6H_3$)(CHCMe$_2$Ph)[BINA(NTs)$_2$], **31**, as a bright yellow powder in 68% yield (eq 2). By ^{1}H NMR (500 MHz, C_6D_6), both the *syn* (Mo=C*H* at 14.49 ppm, J_{CH} = 123 Hz) and *anti* (Mo=C*H* at 15.35 ppm, J_{CH} = 147 Hz) isomers were observed in a ratio of 6:1.



(2)

31

Variable temperature ^{1}H NMR studies (500 MHz, toluene-d_8) of **31** showed that there was no measurable change in the ratio of *syn* to *anti* between 20 °C and 80 °C, and that the compound did not decompose readily at 80 °C (Figure 2.1). The *syn* resonance shifted upfield by 0.2 ppm as the temperature increased to 80 °C; however, this does not appear to correspond to an equilibration of the *syn* and *anti* isomers. Therefore, we propose that there is no exchange between *syn* and *anti* over the course of several minutes at 80 °C. As shown by X-ray crystallography (Section 2.5), a sulfonyl oxygen in one of the tosyl groups is coordinated to molybdenum in complexes of [BINA(NTs)$_2$]H$_2$. Since alkylidene rotation has been observed only when a base dissociates from a five-coordinate adduct of this general type,[27] in this case, alkylidene rotation is effectively blocked by intramolecular sulfonyl coordination.

Complexes containing the more electron-withdrawing imido group N-2-$CF_3C_6H_4$ were synthesized from Mo(N-2-$CF_3C_6H_4$)(CHCMe$_2$Ph)(OTf)$_2$(dme) and Mo(N-2-$CF_3C_6H_4$)(CHCMe$_3$)(OTf)$_2$(dme), both of which were synthesized by John B. Alexander.

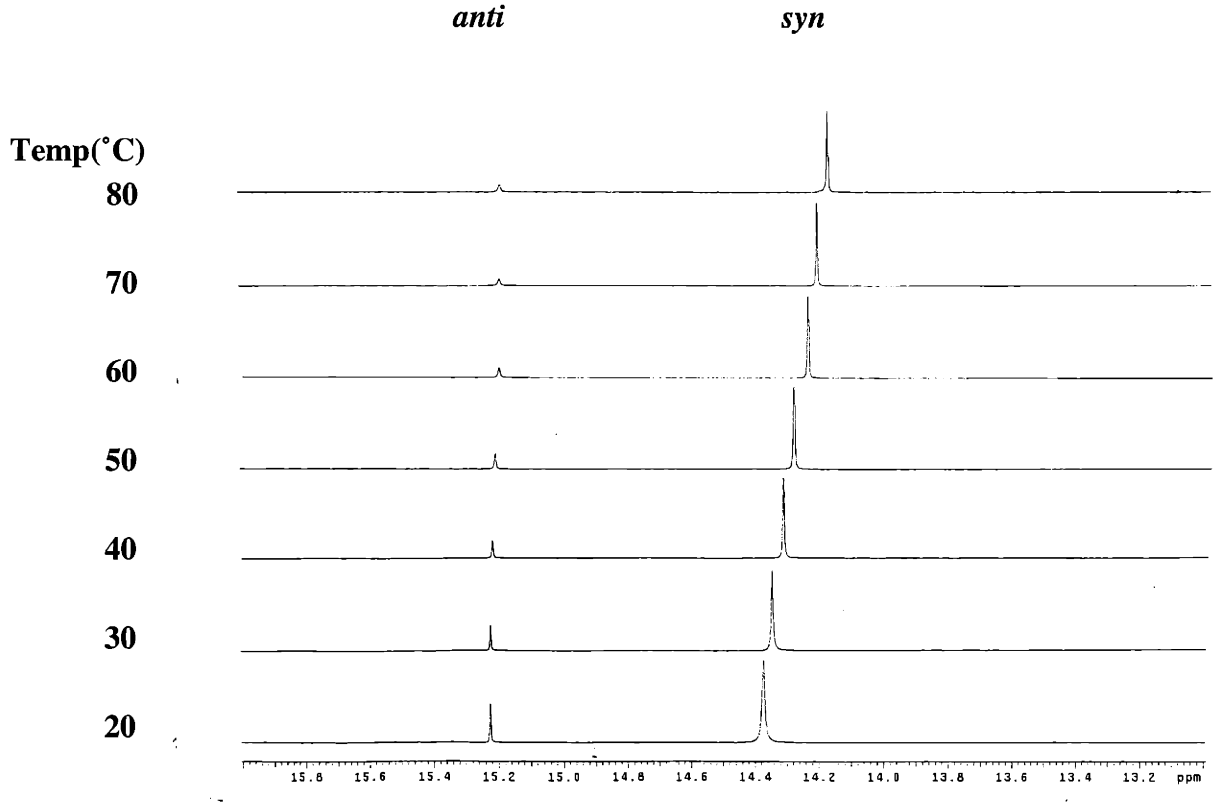
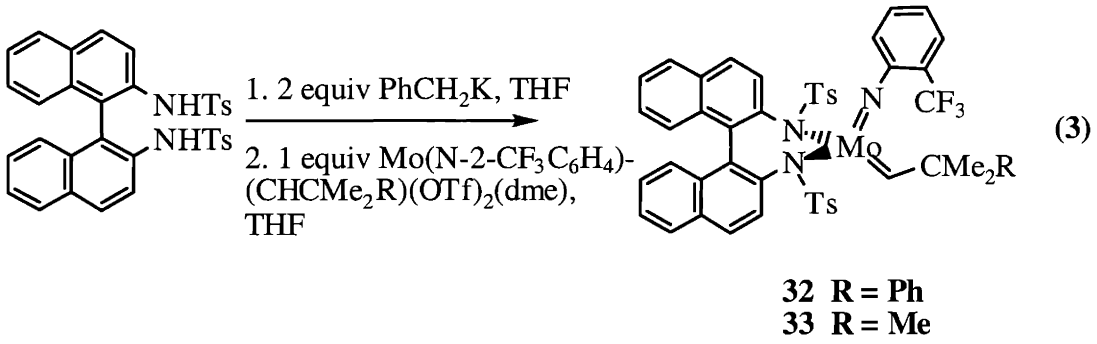


Figure 2.1. Variable temperature ^{1}H NMR (500 MHz, toluene-d_8) of Mo(N-2,6-i-$Pr_2C_6H_3$)($CHCMe_2Ph$)[BINA($NTs)_2$], 31.

Deprotonation of **30** and reaction with Mo(N-2-$CF_3C_6H_4$)($CHCMe_2Ph$)($OTf)_2$(dme) gave Mo(N-2-$CF_3C_6H_4$)($CHCMe_2Ph$)[BINA($NTs)_2$], **32**, as a bright yellow powder in 70% yield (eq 3). By ^1H NMR (500 MHz, C_6D_6), **32** exists primarily as the *syn* isomer (Mo=C*H* at 14.24 ppm, J_{CH} = 125 Hz) with the ratio of *syn*:*anti* (Mo=C*H* at 15.42 ppm) being 50:1.

The neopentylidene analogue of **32** was synthesized using Mo(N-2-$CF_3C_6H_4$)($CHCMe_3$)($OTf)_2$(dme) to give Mo(N-2-$CF_3C_6H_4$)($CHCMe_3$)[BINA($NTs)_2$], **33**, as yellow crystals in 65% yield (eq 3). By ^1H NMR (500 MHz, C_6D_6), **33** exists primarily as the *syn* isomer (Mo=C*H* at 14.14 ppm, J_{CH} = 125 Hz) with a 100:1 ratio of *syn*:*anti* (Mo=C*H* at 15.18 ppm).



(3)

32 R = Ph
33 R = Me

2.2. Reactivity of [BINA($NTs)_2$] Complexes

Attempted metathesis reactions with [BINA($NTs)_2$] complexes **31**, **32** and **33** with ethylene (40 psi) at 80 °C for 2h were unsuccessful in generating the methylidene species; no reaction was observed in any case and there were no changes in the ^1H NMR spectra of these complexes. All three complexes also showed no reactivity with other olefins such as diallyl ether, styrene, and even benzaldehyde, which usually reacts in a Wittig-like fashion with bisalkoxide derivatives of molybdenum imido alkylidene complexes.[5,74] There was no change in the ^1H NMR spectrum of Mo(N-2,6-i-$Pr_2C_6H_3$)($CHCMe_2Ph$)[BINA($NTs)_2$], **31**, in C_6D_6 after 3h at 22 °C in the presence of diallyl ether (5 mol% **31**, 0.1 M diallyl ether), after 13h in the presence of benzaldehyde (0.4 M **31**, 0.4 M benzaldehyde), after 19h in the presence of styrene

(0.1 M **31**, 0.2 M styrene), or after 2h under 40 psi of ethylene at 80 °C (Table 2.1). A similar lack of reactivity was observed for **32** (with diallyl ether, ethylene, or benzaldehyde at 60 °C for 2 h) and **33** (with ethylene, benzaldehyde at 80 °C for 3h, or styrene).

Table 2.1. Summary of Attempted Metathesis Reactions with Mo(N-2,6-i-$Pr_2C_6H_3$)(CHCMe$_2$Ph)[BINA(NTs)$_2$] (31), Mo(N-2-$CF_3C_6H_4$)(CHCMe$_2$Ph)[BINA(NTs)$_2$] (32), and Mo(N-2-$CF_3C_6H_4$)(CHCMe$_3$)[BINA(NTs)$_2$] (33).

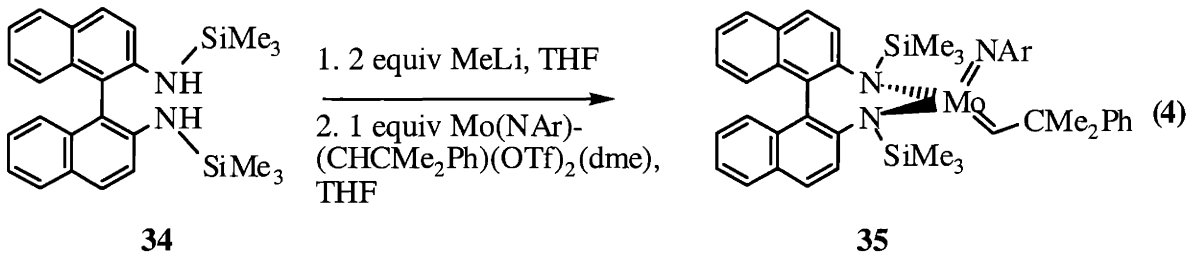
Complex	Substrate	Other Reaction Conditions
31	20 equiv diallyl ether, 0.1M in C_6D_6	
31	40 psi ethylene	80 °C
31	1 equiv benzaldehyde, 0.4M in C_6D_6	
31	2 equiv styrene, 0.1M in C_6D_6	
32	20 equiv diallyl ether, 0.1M in C_6D_6	
32	40 psi ethylene	80 °C
32	8 equiv benzaldehyde, 0.4M in C_6D_6	
32	2 equiv benzaldehyde, 0.1M in C_6D_6	60 °C
33	20 equiv diallyl ether, 0.1M in C_6D_6	
33	40 psi ethylene	80 °C
33	2 equiv styrene, 0.1M in C_6D_6	
33	2 equiv benzaldehyde, 0.4M in C_6D_6	
33	2 equiv benzaldehyde, 0.4M in C_6D_6	80 °C

2.3. Synthesis of Mo(N-2,6-i-$Pr_2C_6H_3$)(CHCMe$_2$Ph)[BINA(NTMS)$_2$]

From the results obtained with complexes **31**, **32** and **33**, it was apparent that [BINA(NTs)$_2$] was not an appropriate choice as a ligand for a molybdenum imido alkylidene catalyst due to stabilization of the complexes resulting from sulfonyl coordination. A second

diamido ligand was examined, incorporating the easily synthesized diamine N,N'-bis(trimethylsilyl)-2,2'-diamino-1,1'-binaphthyl ([BINA(NTMS)$_2$]H$_2$, **34**). Diamine **34** is prepared according to known procedures involving the reaction of 2,2'-diamino-1,1'-binaphthyl with bis(trimethylsilyl)acetamide.[75]

Deprotonation of **34** with methyllithium followed by addition to Mo(N-2,6-i-Pr$_2$C$_6$H$_3$)(CHCMe$_2$Ph)(OTf)$_2$(dme) gave Mo(N-2,6-i-Pr$_2$C$_6$H$_3$)(CHCMe$_2$Ph)[BINA(NTMS)$_2$], **35**, as ruby red crystals in 52% yield (eq 4). Complex **35** existed only as the *syn* isomer by ^{1}H NMR (500 MHz, C$_6$D$_6$) with the Mo=C*H* resonance appearing at 10.50 ppm (J_{CH} = 117 Hz). There was no reaction in the attempted metathesis of diallyl ether, ethylene, benzaldehyde or styrene with **35** (Table 2.2).



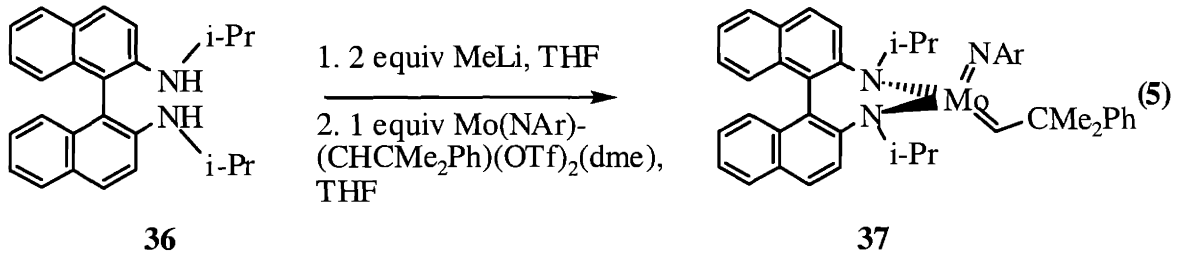
34 **35** (4)

Table 2.2. Summary of Attempted Metathesis Reactions with Mo(N-2,6-i-Pr$_2$C$_6$H$_3$)(CHCMe$_2$Ph)[BINA(NTMS)$_2$] (35).

Complex	Substrate	Other Reaction Conditions
35	20 equiv diallyl ether, 0.1M in C$_6$D$_6$	
35	40 psi ethylene	80 °C
35	1 equiv benzaldehyde, 0.1M in C$_6$D$_6$	
35	2 equiv styrene, 0.1M in C$_6$D$_6$	

2.4. Synthesis of Mo(N-2,6-i-$Pr_2C_6H_3$)(CHCMe$_2$Ph)[BINA(N-i-Pr)$_2$]

The diamine N,N'-bis(*iso*-propyl)-2,2'-diamino-1,1'-binaphthyl ([BINA(N-i-Pr)$_2$]H_2, **36**), was synthesized using known procedures of amine condensation with acetone followed by hydride reduction.[76] Deprotonation of **36** with methyllithium followed by addition to Mo(N-2,6-i-$Pr_2C_6H_3$)(CHCMe$_2$Ph)(OTf)$_2$(dme) gave Mo(N-2,6-i-$Pr_2C_6H_3$)(CHCMe$_2$Ph)[BINA(N-i-Pr)$_2$], **37**, as ruby red crystals in 60% yield (eq 5). By ^{1}H NMR (500 MHz, C_6D_6), this complex existed as the *syn* isomer (Mo=C*H* at 10.46 ppm, J_{CH} = 117 Hz). Complex **37** did not catalyze the RCM of diallyl ether or react with ethylene (40 psi, 80 °C), benzaldehyde or styrene (Table 2.3).



(5)

36 **37**

Table 2.3. Summary of Attempted Metathesis Reactions with Mo(N-2,6-i-$Pr_2C_6H_3$)(CHCMe$_2$Ph)[BINA(N-i-Pr)$_2$] (37).

Complex	Substrate	Other Reaction Conditions
37	10 equiv diallyl ether, 0.1M in C_6D_6	
37	40 psi ethylene	80 °C
37	1 equiv benzaldehyde, 0.1M in C_6D_6	
37	2 equiv styrene, 0.1M in C_6D_6	

2.5. X-ray Crystal Structure of Mo(N-2-$CF_3C_6H_4$)($CHCMe_3$)[BINA($NTs)_2$] and Mo(N-2,6-i-$Pr_2C_6H_3$)($CHCMe_2Ph$)[BINA(N-i-$Pr)_2$].

Single crystals of Mo(N-2-$CF_3C_6H_4$)($CHCMe_3$)[BINA($NTs)_2$], **33**, suitable for X-ray crystallographic analysis were grown from a mixture of THF, ether and pentane at room temperature. The structure of **33** was determined by William M. Davis. Single crystals of Mo(N-2,6-i-$Pr_2C_6H_3$)($CHCMe_2Ph$)[BINA(N-i-$Pr)_2$], **37**, were grown from ether at -30 °C. The structure of **37** was determined by Peter J. Bonitatebus, Jr. Crystallographic data, collection parameters and refinement parameters for **33** and **37** are given in Table 2.4, while selected bond lengths (Å) and angles (°) are given in Table 2.5.

The molecular structure of **33** (Figure 2.2) shows a five-coordinate molybdenum complex that can be described as either a distorted square pyramid or a distorted trigonal bipyramid. In agreement with the ^1H NMR spectrum, the solid state structure of the alkylidene is the *syn* isomer. One sulfonyl oxygen is coordinated to the molybdenum with an Mo-O(22) bond distance of 2.206 Å. The coordinated sulfonyl S(1)-O(22) distance is 1.491 Å, which is longer than the average S-O distance for the non-coordinated oxygens (~1.430 Å). There is also a decrease in the S(1)-N(2) distance to 1.576 Å when compared with bond length of 1.614 Å for the free sulfonyl group. The intramolecular coordination of a sulfonyl group to a transition metal has also been observed for titanium complexes bearing bis(sulfonamido) ligands.[77-79]

The sum of the angles about the two amido nitrogens in Mo(N-2-$CF_3C_6H_4$)($CHCMe_3$)[BINA($NTs)_2$], **33**, shows that both are approximately planar with N(2) ≈ 360° and N(3) ≈ 353° (see Table 2.5). The electron count of molybdenum(VI), including the four σ bonds and the imido and alkylidene π bonds, totals 12. When the overlap of the imido nitrogen lone pair and the additional electron pair from the coordinated sulfonyl group are included, the electron count for molybdenum totals 16. Donation of one planar [BINA($NTs)_2$] nitrogen lone pair to the metal center would bring the total electron count to 18.

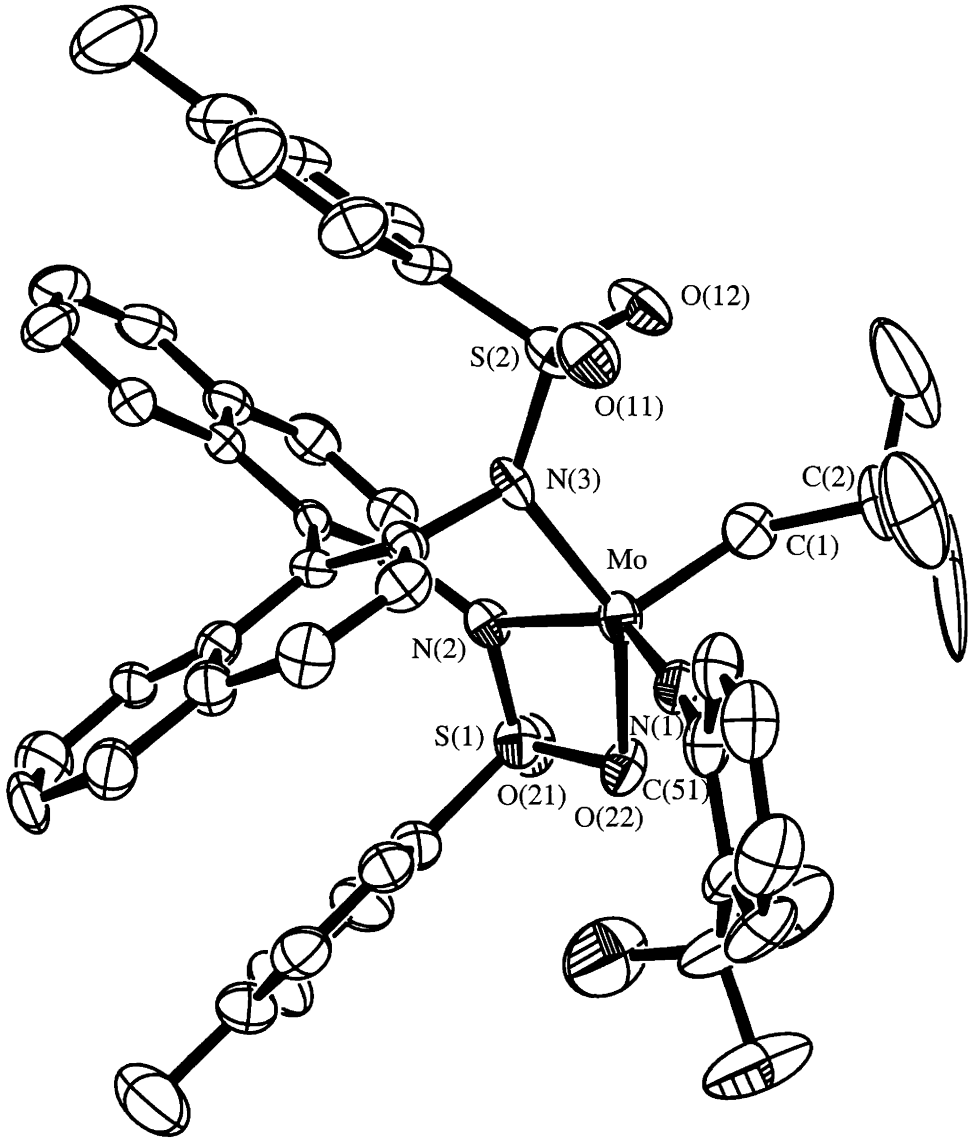


Figure 2.2 ORTEP of Mo(N-2-$CF_3C_6H_4$)($CHCMe_3$)[BINA($NTs)_2$], 33.

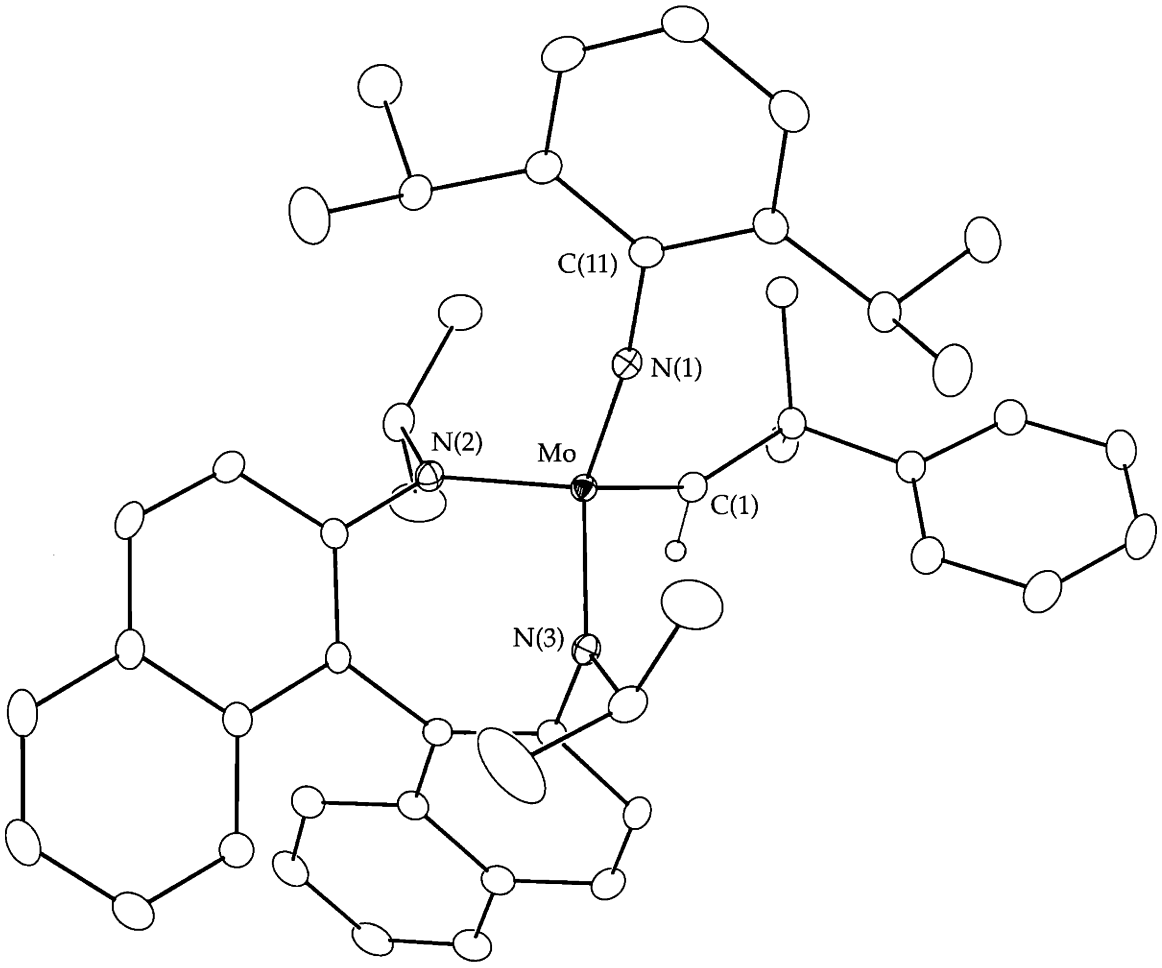


Figure 2.3. ORTEP of Mo(N-2,6-i-Pr$_2$C$_6$H$_3$)(CHCMe$_2$Ph)[BINA(N-i-Pr)$_2$], 37.

Table 2.4. Crystallographic Data, Collection Parameters, and Refinement Parameters for Mo(N-2-$CF_3C_6H_4$)(CHCMe$_3$)[BINA(NTs)$_2$] (33) and Mo(N-2,6-i-$Pr_2C_6H_3$)(CHCMe$_2$Ph)[BINA(N-i-Pr)$_2$] (37).

	[BINA(NTs)$_2$], 33	[BINA(N-i-Pr)$_2$], 37
Empirical formula	$C_{46}H_{40}F_3MoN_3O_4S_2$	$C_{48}H_{55}MoN_3$
Formula Weight	915.87	769.89
Temperature	183(2) K	183(2) K
Wavelength	0.71073 Å	0.71073 Å
Crystal system	Monoclinic	Triclinic
Space group	$P2_1/n$	$P\bar{1}$
Unit cell dimensions	a = 11.5657(6) Å	11.2917(5) Å
	b = 15.0079(8) Å	13.9058(6) Å
	c = 24.9382(13) Å	15.0708(6) Å
	α = 90°	62.54°
	β = 92.6240(10)°	89.923(1)°
	γ = 90°	77.667(1)°
Volume, z	4324.2(4) Å^3, 4	2038.4(2) Å^3, 2
Density (calculated)	1.407 g/cm^3	1.254 g/cm^3
Absorption coefficient	0.459 mm^{-1}	0.358 mm^{-1}
F(000)	1880	812
Crystal size	.2 x .2 x .2 mm	.5 x .5 x .4 mm
θ range for data collection	1.58 to 20.00°	3.06 to 46.48°
Limiting indices	$-12 \le h \le 12$	$-12 \le h \le 9$
	$-15 \le k \le 16$	$-15 \le k \le 11$
	$-13 \le l \le 27$	$-16 \le l \le 16$
Reflections collected	12509	8434
Independent reflections	4027 (R_{int} = 0.0541)	5732 (R_{int} = 0.0338)
Absorption correction	None	Semi-empirical from ψ-scans
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4001 / 0 / 533	5718 / 0 / 469
Goodness-of-fit on F^2	1.339	1.068
Final R indices [I>2σ(I)]	R1 = 0.0638,	R1 = 0.0346,
	wR2 = 0.1324	wR2 = 0.0886
R indices (all data)	R1 = 0.0746,	R1 = 0.0368
	wR2 = 0.1516	wR2 = 0.0922
Extinction coefficient	0.0016(2)	0.0000(8)
Largest diff. peak and hole	0.382 and -0.453 eÅ^{-3}	0.800 and -0.542 eÅ^{-3}

Table 2.5. Selected bond lengths (Å) and angles (°) for Mo(N-2-$CF_3C_6H_4$)(CHCMe$_3$)[BINA(NTs)$_2$] (33) and Mo(N-2,6-i-$Pr_2C_6H_3$)(CHCMe$_2$Ph)[BINA(N-i-Pr)$_2$] (37).

		[BINA(NTs)$_2$], 33		[BINA(N-i-Pr)$_2$], 37	
Mo-N_{imido}	Mo-N(1)	1.737(7)	Mo-N(1)	1.747(2)
Mo-$C_{alkylidene}$	Mo-C(1)	1.861(8)	Mo(1)-C(1)	1.904(3)
Mo-N_{amide}	Mo-N(2)	2.158(6)	Mo-N(2)	2.004(2)
Mo- N_{amide}	Mo-N(3)	2.076(6)	Mo-N(3)	1.981(2)
Mo-$O_{sulfonyl}$	Mo-O(22)	2.206(5)		
$C_{alkylidene}$-CMe$_3$	C(1)-C(2)	1.521(11)	C(1)-C(2)	1.523(4)
N_{imido}-C_{aryl}	N(1)-C(51)	1.408(10)	N(1)-C(11)	1.400(4)
S-$O_{coordinated}$	S(1)-O(22)	1.491(5)		
S-$O_{uncoordinated}$	S(1)-O(21)	1.430(5)		
	S(2)-O(11)	1.436(6)		
	S(2)-O(12)	1.425(5)		
N_{amide}-S	N(2)-S(1)	1.576(6)		
	N(3)-S(2)	1.614(6)		
N_{imido}-Mo-$C_{alkylidene}$	N(1)-Mo-C(1)	101.3(3)	N(1)-Mo-C(1)	104.96(11)
Mo=C-C	Mo-C(1)-C(2)	143.6(7)	Mo-C(1)-C(2)	144.0(2)
Mo=N-C_{imido}	Mo-N(1)-C(30)	171.3(5)	Mo-N(1)-C(11)	172.2(2)
N_{amide}-Mo-N_{amide}	N(2)-Mo-N(3)	82.2(2)	N(2)-Mo-N(3)	107.00(9)
planar N_{amide}	Mo-N(2)-C(21)	134.8(5)	Mo-N(2)-C(23)	112.2(2)
	Mo-N(2)-S(1)	98.5(3)	Mo-N(2)-C(43)	132.8(2)
	S(1)-N(2)-C(21)	126.5(5)	C(23)-N(2)-C(43)	115.0(2)
		359.8		360.0
	Mo-N(3)-C(11)	105.8(4)	Mo-N(3)-C(42)	106.4(2)
	Mo-N(3)-S(2)	127.5(3)	Mo-N(3)-C(46)	136.4(2)
	S(2)-N(3)-C(11)	119.5(5)	C(42)-N(3)-C(46)	116.9(2)
		352.8		359.7

This could account for the observed non-reactivity and high stability of these compounds in the presence of olefins. The fact that there is no exchange of the *syn* and *anti* isomers, even at elevated temperatures, also indicates that the coordinated sulfonyl group contributes to a highly stable, unreactive compound.

The structure of Mo(N-2,6-i-$Pr_2C_6H_3$)(CHCMe$_2$Ph)[BINA(N-i-Pr)$_2$], **37** (Figure 2.3), also shows that the amido nitrogens are planar, with the sum of the angles about both N(2) and N(3) ≈ 360°. The geometry of **37** is pseudo-tetrahedral and the *syn* isomer selectively crystallized. The average Mo-N_{amide} bond length in **37** is 1.993Å, shorter than the average for complex **33** (2.118 Å), indicating greater donation from the nitrogen π electrons to the metal in **37**, when the coordinating sulfonyl group is replaced with an isopropyl group. Counting the four σ bonds, the imido and alkylidene π bonds, overlap of the imido nitrogen lone pair and donation from both of the perpendicular, planar [BINA(N-i-Pr)$_2$] nitrogen lone pairs to the metal, the total electron count for molybdenum is 18. The lack of reactivity of the [BINA(NTs)$_2$] complexes **31**, **32**, and **33** is attributed to sulfonyl coordination, as shown in the X-ray crystal structure of **33**. Similarly, the lack of reactivity in Mo(N-2,6-i-$Pr_2C_6H_3$)(CHCMe$_2$Ph)[BINA(NTMS)$_2$], **35**, and Mo(N-2,6-i-$Pr_2C_6H_3$)(CHCMe$_2$Ph)[BINA(N-i-Pr)$_2$], **37**, could be explained by the X-ray crystal structure of **37**. Although steric hindrance near the metal is severe in all [BINA(NR)$_2$] type complexes, we propose that electronic factors are largely to blame for the lack of reactivity. The [BINA(NTs)$_2$] and [BINA(N-i-Pr)$_2$] complexes, and we assume also the [BINA(NTMS)$_2$] complex, are 18 electron species with no low energy LUMO to which an incoming olefin can bind.

The lack of reactivity of these [BINA(NR)$_2$] complexes contrasts with the high reactivity of molybdenum imido alkylidene complexes containing bisaryloxide ligands. The two main differences are that bisaryloxides are much less sterically encumbered near the metal and an alkoxide oxygen is also likely to be a poorer σ and π donor than an amido nitrogen, thereby leaving the metal more electron deficient.

CONCLUSIONS

In summary, a new class of molybdenum imido alkylidene complexes bearing 2,2'-diamido-1,1'-binaphthyl derivatives as ligands were synthesized. The derivatizations included tosyl, isopropyl and trimethylsilyl groups. None of these complexes proved to be effective metathesis catalysts, even when exposed to high pressures of ethylene (40 psi). The molybdenum complexes are stabilized by donation from the diamido nitrogen lone pairs, and the metal center does not exhibit the electrophilicity required to induce catalytic metathesis processes such as RCM.

EXPERIMENTAL

General Details. All experiments were conducted under nitrogen in a Vacuum Atmospheres drybox or using standard Schlenk techniques. THF, toluene, ether, and pentane were sparged with nitrogen and passed through alumina columns. Benzene was distilled from sodium benzophenone ketyl. Dichloromethane was distilled from CaH_2. 2,2'-Diamino-1,1'-binaphthyl,[68] benzyl potassium,[66] $[BINA(NTMS)_2]H_2$ (**34**),[75] $[BINA(N\text{-}i\text{-}Pr)_2]H_2$ (**36**),[76] $Mo(N\text{-}2,6\text{-}i\text{-}Pr_2C_6H_3)(CHCMe_2Ph)(OTf)_2(dme)$,[16] $Mo(N\text{-}2\text{-}CF_3C_6H_4)(CHCMe_2Ph)(OTf)_2(dme)$[24] and $Mo(N\text{-}2\text{-}CF_3C_6H_4)(CHCMe_3)(OTf)_2(dme)$[24] were prepared according to literature procedures. 2,2'-Diamino-1,1'-binaphthyl was a gift from Robert Baumann, $[BINA(NTs)_2]H_2$ was synthesized by S. Sherry Zhu, and $Mo(N\text{-}2\text{-}CF_3C_6H_4)(CHCMe_2Ph)(OTf)_2(dme)$ and $Mo(N\text{-}2\text{-}CF_3C_6H_4)(CHCMe_3)(OTf)_2(dme)$ were gifts from John B. Alexander. All other reagents were used as received from commercial sources. C_6D_6 and $CDCl_3$ were sparged with nitrogen and stored over 4 Å molecular sieves. ^1H and ^{13}C NMR data are listed in parts per million downfield from tetramethylsilane and were referenced using the residual protio solvent resonance. ^{19}F NMR data were referenced externally using $CFCl_3$ in $CHCl_3$ as a standard (0 ppm). ^1H NMR spectra of **31-33**, **35** and **37** showed mixtures of *syn*:*anti* isomers in ratios described in the text; herein only the major isomers are described. Routine NMR coupling constants are not reported. Spectra were obtained at room temperature. Elemental analyses were performed by H. Kolbe

Laboratories, Mülheim an der Ruhr, Germany. High resolution mass spectral analyses were performed by the Massachusetts Institute of Technology Department of Chemistry Instrumentation Facility.

[BINA(NTs)$_2$]H$_2$ (30)

p-Toluenesulfonyl chloride (13.1 g, 68.7 mmol) was added to a solution of 2,2'-diamino-1,1'-binaphthyl (5.00 g, 17.5 mmol) in pyridine (200 mL). After stirring overnight at room temperature, methanol was added to give a white precipitate that was isolated by filtration, dried *in vacuo* and recrystallized from CH_2Cl_2 to give **30** as a white powder (10.37 g, 100%). ^{1}H NMR (300 MHz, C_6D_6): 8.37 (d, 2, Ar*H*), 7.58 (d, 2, Ar*H*), 7.48 (d, 4, Ar*H*), 7.41 (d, 2, Ar*H*), 6.97 (t, 2, Ar*H*), 6.64 (d, 4, Ar*H*), 6.59 (t, 2, Ar*H*), 6.51 (d, 2, Ar*H*), 6.10 (s, 2, N*H*), 1.92 (s, 6, ArC*H*$_3$). ^{13}C NMR (125.8 MHz, $CDCl_3$): 144.35, 135.42, 134.01, 132.00, 130.79, 130.62, 129.71, 128.17, 127.57, 127.00, 125.29, 124.19, 117.99, 117.32, 21.43. HRMS Calcd for $C_{34}H_{28}N_2S_2O_4$: 592.149051; Found: 592.1480.

Mo(N-2,6-i-Pr$_2$C$_6$H$_3$)(CHCMe$_2$Ph)[BINA(NTs)$_2$] (31)

Benzyl potassium (120 mg, 0.92 mmol) was dissolved in THF (1 mL) and added to **30** (218 mg, 0.37 mmol) in THF (3 mL) until the solution was pale orange. A solution of Mo(N-2,6-i-Pr$_2$C$_6$H$_3$)(CHCMe$_2$Ph)(OTf)$_2$(dme) (291 mg, 0.37 mmol) in THF (2 mL) was then added, turning the reaction mixture dark red. After stirring for 15h, the solvent was evaporated and the resulting solid extracted with benzene. This solution was filtered through Celite, the benzene evaporated and the resulting solid dissolved in a minimal amount of ether. Pentane was added until the solution was barely cloudy and it was then stored at -30 °C to give **31** as a canary yellow powder (248 mg, 67.7%). ^{1}H NMR (500 MHz, C_6D_6): (major isomer) 14.49 (s, 1, Mo=C*H*, J_{CH} = 123 Hz), 8.31 (d, 1, Ar*H*), 7.65 (d, 2, Ar*H*), 7.40 (m, 3, Ar*H*), 7.25 (m, 3, Ar*H*), 7.05 (m, 9, Ar*H*), 6.83 (m, 2, Ar*H*), 6.48 (m, 4, Ar*H*), 6.08 (br m, 2, Ar*H*), 5.90 (d, 2, Ar*H*), 4.33 (sept, 2, C*H*Me$_2$), 2.33 (s, 3, ArC*H*$_3$), 2.09 (s, 3, ArC*H*$_3$), 1.57 (d, 6, CH(C*H*$_3$)$_2$), 1.52 (d, 6, CH(C*H*$_3$)$_2$),

1.19 (s, 3, CHC(CH_3)$_2$Ph), 1.17 (s, 3, CHC(CH_3)$_2$Ph). ^{13}C NMR (125.8 MHz, C_6D_6): (mixture of isomers) 329.55, 310.98, 154.24, 152.80, 150.64, 149.80, 148.48, 147.84, 144.47, 144.28, 141.27, 140.63, 140.13, 138.93, 138.78, 137.57, 137.27, 135.91, 135.69, 134.59, 134.43, 134.23, 134.00, 133.25, 133.19, 133.06, 132.39, 132.26, 132.06, 131.71, 131.44, 130.03, 129.86, 129.52, 129.40, 129.20, 129.11, 128.92, 128.54, 128.20, 127.93, 127.89, 127.77, 127.43, 127.27, 126.98, 126.92, 126.48, 126.37, 126.22, 126.15, 126.04, 124.76, 124.68, 127.27, 123.58, 122.41, 121.93, 68.22, 57.08, 55.30, 33.73, 30.68, 29.84, 29.31, 28.95, 28.54, 26.24, 25.84, 25.05, 24.95, 24.65, 24.61, 21.38. Anal. Calcd. for $MoC_{56}H_{55}N_3O_4S_2$: C 67.66, H 5.58, N 4.23; Found: C 67.38, H 5.62, N 4.28.

Mo(N-2-$CF_3C_6H_4$)(CHCMe$_2$Ph)[BINA(NTs)$_2$] (32)

Benzyl potassium (219 mg, 1.7 mmol) was dissolved in THF (1 mL) and added to a suspension of **30** (399 mg, 0.67 mmol) in THF (3 mL) until the solution was pale orange. A solution of Mo(N-2-$CF_3C_6H_4$)(CHCMe$_2$Ph)(OTf)$_2$(dme) (500 mg, 0.67 mmol) in THF (2 mL) was then added, turning the reaction mixture dark red. After being stirred for 20h, the solvent was evaporated and the solid extracted with benzene. The resulting solution was filtered through Celite, the benzene evaporated and the resulting solid dissolved in a minimal amount of ether. Pentane was added until the solution was barely cloudy and it was then stored at -30 °C to give **32** as a yellow powder (460 mg, 69.9%). ^{1}H NMR (500 MHz, C_6D_6): (major isomer) 14.24 (s, 1, Mo=C*H*, J_{CH} =125 Hz), 8.35 (d, 1, Ar*H*), 8.24 (d, 1, Ar*H*), 8.20 (br s, 1, Ar*H*), 7.70 (d, 2, Ar*H*), 7.49 (d, 1, Ar*H*), 7.45 (d, 1, Ar*H*), 7.38 (d, 1, Ar*H*), 7.33 (d, 1, Ar*H*), 7.27 (d, 2, Ar*H*), 7.20 (t, 2, Ar*H*), 7.12 (d, 1, Ar*H*), 7.09 (t, 1, Ar*H*), 6.97 (br t, 3, Ar*H*), 6.90 (t, 2, Ar*H*), 6.67 (t, 1, Ar*H*), 6.43 (t, 1, Ar*H*), 6.33 (br d, 2, Ar*H*), 6.26 (d, 1, Ar*H*), 5.98 (d, 2, Ar*H*), 5.93 (br s, 2 Ar*H*), 2.25 (s, 3, ArCH_3), 1.92 (s, 3, ArCH_3), 1.60 (s, 3, CHC(CH_3)$_2$Ph), 1.52 (s, 3, CHC(CH_3)$_2$Ph). ^{13}C NMR (125.8 MHz, C_6D_6): 311.80, 153.02, 149.17, 144.31, 141.42, 139.40, 138.67, 137.00, 134.76, 134.55, 134.23, 133.06, 132.46, 131.76, 131.48, 130.35, 129.60, 129.55, 129.32, 129.01, 128.81, 128.68, 128.49, 128.30, 128.10, 127.93, 127.87, 127.56, 126.91, 126.85, 126.32, 126.23,

126.19, 126.14, 125.91, 124.82, 66.26, 58.18, 33.23, 28.95, 24.50, 21.26, 15.96. ^{19}F NMR (282 MHz, C_6D_6): -61.75 (s) Anal. Calcd. for $MoC_{51}H_{42}N_3F_3O_4S_2$: C 62.64, H 4.33, N 4.30; Found: C 62.66, H 4.33, N 4.21.

Mo(N-2-$CF_3C_6H_4$)(CHCMe$_3$)[BINA(NTs)$_2$] (33)

Benzyl potassium (219 mg, 1.7 mmol) was dissolved in THF (1 mL) and added to a suspension of **30** (400 mg, 0.67 mmol) in THF (3 mL) until the solution was pale orange. A solution of Mo(N-2-$CF_3C_6H_4$)(CHCMe$_3$)(OTf)$_2$(dme) (481 mg, 0.67 mmol) in THF (2 mL) was then added, turning the reaction mixture dark red. After being stirred for 20h, the solvent was evaporated and the solid extracted with benzene. The solution was filtered through Celite, the benzene evaporated and the resulting solid dissolved in a minimal amount of ether from which **33** spontaneously crystallized. The precipitate was isolated and washed with ether to give the product as a yellow powder (404 mg, 65.3%). ^{1}H NMR (500 MHz, C_6D_6): (major isomer) 14.13 (s, 1, Mo=C*H*, J_{CH} = 125 Hz), 8.40 (m, 3, Ar*H*), 7.54 (d, 1, Ar*H*), 7.46 (d, 1, Ar*H*), 7.39 (d, 1, Ar*H*), 7.33 (d, 1, Ar*H*), 7.31 (d, 2, Ar*H*), 7.12 (t, 2, Ar*H*), 7.03 (br d, 2, Ar*H*), 6.90 (m, 2, Ar*H*), 6.64 (t, 1, Ar*H*), 6.42 (m, 1, Ar*H*), 6.35 (br m, 2, Ar*H*), 6.25 (d, 1, Ar*H*), 5.99 (d, 2, Ar*H*), 5.94 (br d, 2, Ar*H*), 1.58 (s, 3, ArCH_3), 1.56 (s, 9, C(CH_3)$_3$), 1.51 (s, 3, ArCH_3). ^{13}C NMR (125.8 MHz, C_6D_6): 315.08, 153.37, 144.20, 141.37, 139.91, 138.60, 137.15, 134.79, 134.32, 133.08, 133.02, 132.27, 131.74, 131.37, 130.18, 129.60, 129.30, 128.78, 128.67, 128.09, 128.04, 127.86, 126.71, 126.31, 126.28, 126.09, 125.80, 125.29, 124.75, 122.91, 68.16, 51.71, 31.37, 26.15, 21.46, 21.22. ^{19}F NMR (282 MHz, C_6D_6): -61.96 (s). Anal. Calcd. for $MoC_{46}H_{40}N_3S_2O_4F_3$: C 60.32, H 4.40, N 4.59; Found: C 60.22, H 4.52, N 4.51.

Mo(N-2,6-i-$Pr_2C_6H_3$)(CHCMe$_2$Ph)[BINA(NTMS)$_2$] (35)

Methyllithium (1.60M in ether, 0.52 mL, 0.84 mmol) was added dropwise to [BINA(NTMS)$_2$]H_2 (**34**) (164 mg, 0.38 mmol) in THF (2 mL) and the solution was stirred until no further methane evolution was observed. Mo(N-2,6-i-$Pr_2C_6H_3$)(CHCMe$_2$Ph)(OTf)$_2$(dme)

(302 mg, 0.38 mmol) in THF (1 mL) was then added and the dark red solution was stirred for 12h. The solvent was evaporated and the resulting solid extracted with benzene and filtered through Celite. The benzene was evaporated to give a red solid that was dissolved in a mixture of ether and pentane and stored at -30 °C. The product **35** was isolated as ruby red crystals (164 mg, 51.7%). ^{1}H NMR (500 MHz, C_6D_6): 10.50 (s, 1, Mo=C*H*, J_{CH} = 117 Hz), 7.70 (d, 2, Ar*H*), 7.65 (d, 2, Ar*H*), 7.64 (d, 1, Ar*H*), 7.61 (d, 1, Ar*H*), 7.55 (d, 2, Ar*H*), 7.35 (d, 1, Ar*H*), 7.30 (m, 3, Ar*H*), 7.15 - 7.00 (m, 6, Ar*H*), 6.95 (t, 2, Ar*H*), 4.19 (sept, 2, C*H*(CH_3)$_2$), 1.94 (s, 3, C(C*H*$_3$)$_2$Ph), 1.29 (d, 6, CH(C*H*$_3$)$_2$), 1.28 (s, 3, C(C*H*$_3$)$_2$Ph), 1.19 (d, 6, CH(C*H*$_3$)$_2$), -0.06 (s, 9, Si(C*H*$_3$)$_3$), -0.13 (s, 9, Si(C*H*$_3$)$_3$). ^{13}C NMR (125.8 MHz, C_6D_6): 269.62, 153.65, 151.30, 149.74, 145.50, 145.41, 135.16, 134.88, 133.89, 132.28, 132.03, 131.63, 131.48, 131.06, 129.65, 129.61, 129.09, 129.01, 128.78, 128.62, 127.61, 127.47, 127.25, 127.03, 126.69, 126.37, 125.75, 125.22, 124.17, 54.15, 33.82, 31.50, 28.15, 25.56, 25.37, 3.01, 2.67. Anal. Calcd. for $MoC_{48}H_{59}N_3Si_2$: C 69.29, H 7.15, N 5.05; Found: C 68.81, H 7.07, N 4.83.

Mo(N-2,6-i-Pr$_2$C$_6$H$_3$)(CHCMe$_2$Ph)[BINA(N-i-Pr)$_2$] (37)

Methyllithium (1.57M in ether, 0.80 mL, 1.25 mmol) was added dropwise to a solution of [BINA(N-i-Pr)$_2$]H$_2$ (**36**) (210 mg, 0.57 mmol) in THF (4 mL). After no further methane evolution was observed, a solution of Mo(N-2,6-i-Pr$_2$C$_6$H$_3$)(CHCMe$_2$Ph)(OTf)$_2$(dme) (450 mg, 0.57 mmol) in THF (2 mL) was added and the mixture turned dark red. After stirring overnight (18h), the solvent was evaporated, the residue dissolved in benzene and the solution filtered through Celite. The benzene was evaporated and the resulting red foam was dissolved in ether (2 mL) and stored at -30 °C to give the product **37** as ruby red crystals (264 mg, 60.3%). ^{1}H NMR (500 MHz, C_6D_6): 10.46 (s, 1, Mo=C*H*, J_{CH} = 117 Hz), 7.81 (d, 1, Ar*H*), 7.79 (d, 1, Ar*H*), 7.74 (d, 1, Ar*H*), 7.68 (d, 1, Ar*H*), 7.63 (d, 1, Ar*H*), 7.60 (d, 1, Ar*H*), 7.54 (d, 2, Ar*H*), 7.27 (d, 2, Ar*H*), 7.25 (d, 2, Ar*H*), 7.13 (d, 1, Ar*H*), 7.11 - 7.04 (m, 4, Ar*H*), 6.94 - 6.90 (m, 3, Ar*H*), 4.22 (br sept, 2, C*H*Me$_2$ imido), 3.99 (br sept, 1, NC*H*Me$_2$), 3.92 (br sept, 1, NC*H*Me$_2$), 1.97 (s, 3, CHC(C*H*$_3$)$_2$Ph), 1.41 (s, 3, CHC(C*H*$_3$)$_2$Ph), 1.21 (br m, 12, CH(C*H*$_3$)$_2$ imido), 1.06 (br d, 3,

NCH(CH_3)$_2$), 1.02 (br d, 3, NCH(CH_3)$_2$), 0.95 (br d, 3, NCH(CH_3)$_2$), 0.72 (br d, 3, NCH(CH_3)$_2$). ^{13}C NMR (125.8 MHz, C_6D_6): 268.83, 153.56, 151.59, 151.40, 146.00, 144.94, 134.60, 134.53, 133.49, 131.67, 131.38, 131.26, 130.33, 130.21, 129.86, 128.76, 128.68, 128.49, 128.29, 127.17, 127.01, 126.79, 126.41, 126.18, 125.50, 125.13, 123.81, 61.99, 61.55, 53.07, 33.55, 32.15, 28.39, 28.14, 26.73, 25.87, 25.09, 24.81, 23.63. Anal. Calcd. for $MoC_{48}H_{55}N_3$: C 74.88, H 7.20, N 5.46; Found: C 75.08, H 7.18, N 5.34.

Representative Procedure for Reaction of [BINA(NR)$_2$] Complexes with Ethylene

Mo(N-2-$CF_3C_6H_4$)(CHCMe$_2$Ph)[BINA(NTs)$_2$] (**32**) (15 mg) was dissolved in ~1 mL C_6D_6 and put under an atmosphere of 40 psi ethylene in a sealed reaction flask and heated to 80 °C with an oil bath. After 5h, the reaction flask was opened and the solution transferred to an NMR tube. The progress of the reaction was determined by ^{1}H NMR (500 MHz, C_6D_6).

Representative Procedure for Reaction of [BINA(NR)$_2$] Complexes with Styrene, Benzaldehyde or Diallyl Ether

Mo(N-2-$CF_3C_6H_4$)(CHCMe$_2$Ph)[BINA(NTs)$_2$] (**32**) (10 mg) was dissolved in ~1 mL C_6D_6 and diallyl ether (20 mg) was added. The reaction mixture was stirred in a loosely capped vial overnight. The solution was then transferred to an NMR tube and the progress of the reaction was determined by ^{1}H NMR (500 MHz, C_6D_6).

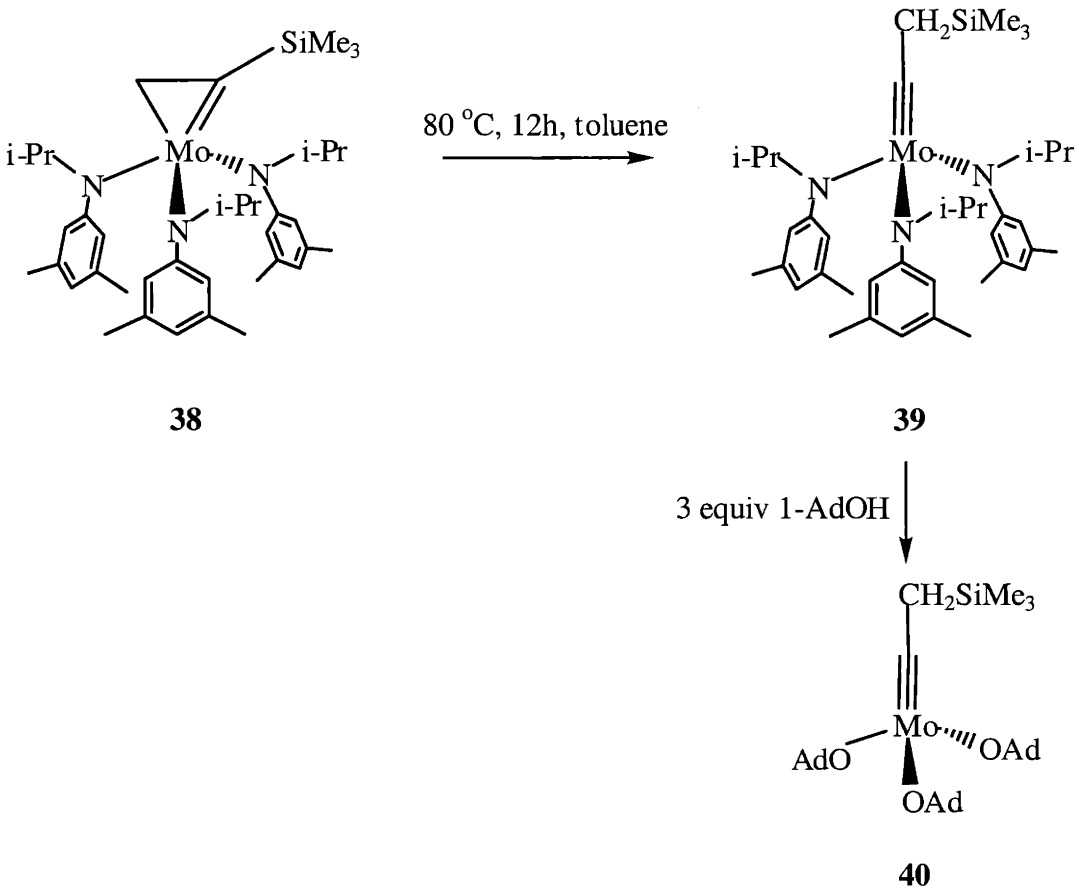
Chapter 3

SYNTHESIS OF MOLYBDENUM ALKYLIDYNE BIPHEN COMPLEXES

INTRODUCTION

While a general synthetic route towards molybdenum imido alkylidene bisaryloxide complexes exists (see Scheme 1.3),[16] similar synthetic pathways towards molybdenum alkyli*dyne* complexes are not as practical. The tungsten alkylidyne complex $W(CCMe_3)(OCMe_3)_3$ is a well-known alkyne metathesis catalyst, easily prepared by the reaction of ditungsten hexa-*tert*-butoxide with excess $MeC{\equiv}CCMe_3$.[80] However, the analogous molybdenum complex, $Mo(CCMe_3)(OCMe_3)_3$, is an impractical catalyst for alkyne metathesis because the synthesis is low yielding and less facile.[81]

Recently, the three-coordinate molybdenum trisanilide complex, $Mo[N(CMe_3)Ar"]_3$ (Ar" = 3,5-$Me_2C_6H_3$), was shown to metathesize alkynes (by an unknown mechanism) in the



Scheme 3.1. Synthesis of $Mo(CCH_2SiMe_3)(OAd)_3$, 40.

presence of dichloromethane.[82] The Cummins group then developed a facile synthetic route towards molybdenum alkylidyne trisalkoxide complexes beginning with molybdenum trisanilide precursors (Scheme 3.1).[83] The η^2-vinyl complex, Mo(η^2-$H_2CCSiMe_3$)[N(i-Pr)Ar"]$_3$, **38**, was heated to 80 °C in toluene, giving the alkylidyne complex Mo(CCH_2SiMe_3)[N(i-Pr)Ar"]$_3$, **39**, by trimethylsilyl group transfer. Subsequent treatment with 3 equiv 1-adamantanol results in the alcoholysis of the Mo-N_{amide} bonds to give the complex Mo(CCH_2SiMe_3)(OAd)$_3$, **40**, in 88% yield. This complex was shown to catalyze alkyne metathesis. Our objective was to react diols such as [±-biphen]H_2 with **39** to generate molybdenum amido alkylidyne bisaryloxide complexes.

RESULTS AND DISCUSSION

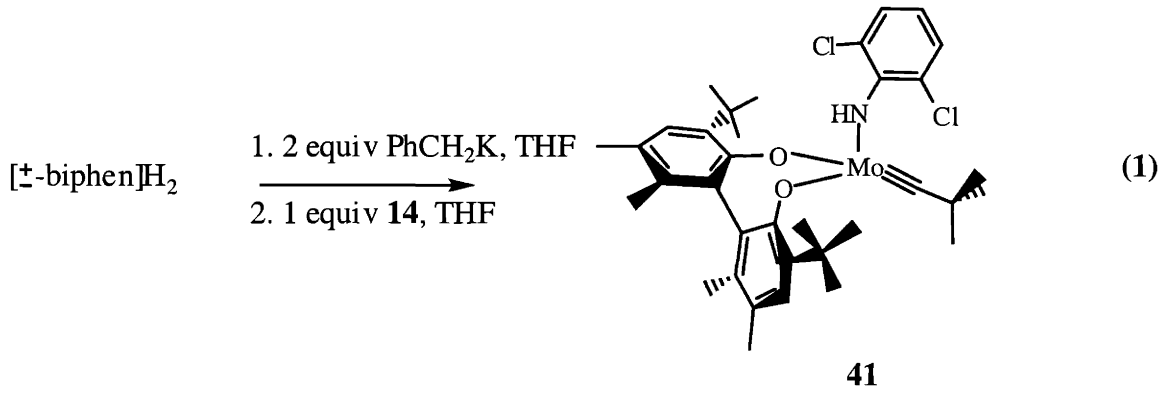
3.1. Synthesis of Molybdenum 2,6-Dichloroarylamido Alkylidyne Biphen Complexes

Molybdenum amido alkylidyne complexes have been previously prepared by reaction of Mo($CCMe_3$)Cl_3(dme) with HN(2,6-i-$Pr_2C_6H_3$)($SiMe_3$) to give Mo(NH-2,6-i-$Pr_2C_6H_3$)($CCMe_3$)Cl_2(dme).[84] This product was then converted to the imido alkylidene product, Mo(N-2,6-i-$Pr_2C_6H_3$)($CHCMe_3$)Cl_2(dme), using a catalytic amount of Et_3N.

The following results describe two cases in which attempted synthesis of a molybdenum imido alkylidene biphen product instead yielded the amido alkylidyne isomer. In both cases, the particular conditions leading to these unexpected results could not be reproduced and extensive study towards elucidating the cause of alkylidyne versus alkylidene formation did not shed light on the factors involved. Subsequent attempts to repeat these reactions generated only alkylidene or mixtures of alkylidene/alkylidyne products.

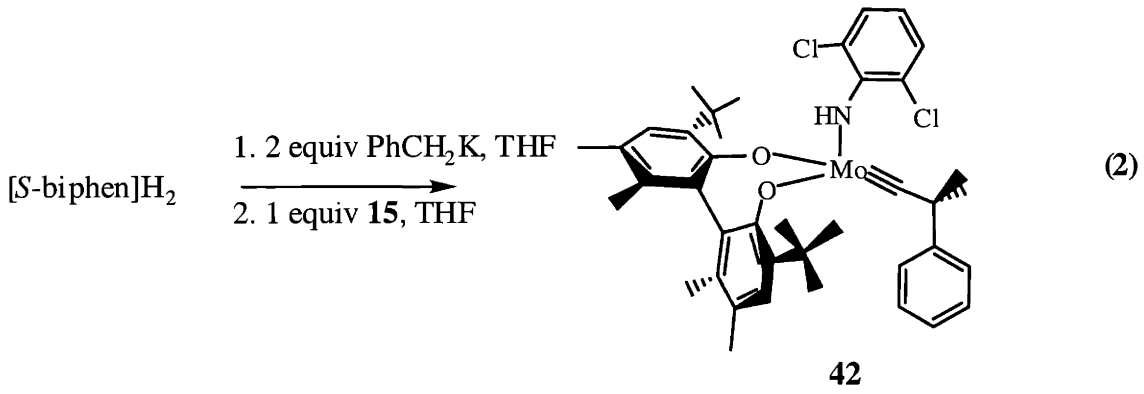
As shown in Section 1.3, Mo(N-2,6-$Cl_2C_6H_3$)($CHCMe_3$)(±-biphen)(THF), **16rac**, is synthesized by reaction of deprotonated [±-biphen]H_2 with Mo(N-2,6-$Cl_2C_6H_3$)($CHCMe_3$)($OTf)_2$(dme), **14**. In one case, however, the isolated product of the reaction was instead Mo(NH-2,6-$Cl_2C_6H_3$)($CCMe_3$)(±-biphen), **41**. Complex **41** was isolated as a yellow

powder in 17% yield (eq 1). The ^{1}H NMR spectrum (500 MHz, C_6D_6) of **41** shows a singlet resonance at 11.73 ppm corresponding to the N*H* proton. The *meta* protons on the arylimido ligand appear as a broad singlet resonance at 6.69 ppm, indicating that there is slowed rotation of the imido aryl ring. As shown in Section 3.2, the X-ray crystal structure of the analogous alkylidyne complex, Mo(NH-2,6-$Cl_2C_6H_3$)(CCMe$_2$Ph)(*S*-biphen) shows that the amido ligand is bent to 134° (compared with 150° for Mo(N-2,6-$Cl_2C_6H_3$)(CHCMe$_3$)(*S*-biphen)(THF), **16**) and the Mo-Cl distance is ~3Å. While this distance does not indicate a bonding interaction in the solid-state, in solution there could be a dative interaction of alternating arylimido chlorines with molybdenum, which would slow the rotation of the arylimido ring. This type of "light" coordination of a 2,6-dichlorophenyl group to a metal has also been postulated for the cationic zirconium complex, {[(2,6-$Cl_2C_6H_3NCH_2CH_2)_2$NMe]ZrMe}$^+$.[85] Unfortunately, the isolated yield of **41** was only 32 mg, which did not allow for further study after the sample had been fully characterized.



41 **(1)**

The second case in which an amido alkylidyne product was unexpectedly isolated occurred in the attempted synthesis of Mo(N-2,6-$Cl_2C_6H_3$)(CHCMe$_2$Ph)(*S*-biphen). [*S*-Biphen]H_2 was deprotonated and added to Mo(N-2,6-$Cl_2C_6H_3$)(CHCMe$_2$Ph)(OTf)$_2$(THF)$_x$, **15**, to give the alkylidyne product Mo(NH-2,6-$Cl_2C_6H_3$)(CCMe$_2$Ph)(*S*-biphen), **42**, as a yellow powder in 38% yield (eq 2). Subsequent attempts to reproduce this result were unsuccessful, resulting in mixtures of alkylidene and alkylidyne products.



(2)

42

The alkylidyne structure of **42** was confirmed by ^{1}H NMR (500 MHz, C_6D_6) which showed the N*H* proton resonance at 11.59 ppm. As observed for **41**, the *meta* protons on the arylimido group of **42** also appeared as a broad singlet resonance (6.66 ppm). By ^{1}H coupled ^{13}C NMR (125 MHz, C_6D_6), the resonance corresponding to the Mo-C was a singlet at 322.13 ppm Confirmation of the molecular structure of **42** was obtained by X-ray crystallographic study of single crystals of the complex (Section 3.2).

Previous reports from our group postulated that alkylidyne formation occurred only when imido ligands were not substituted in *both ortho* positions (such as the N-2-$CF_3C_6H_4$ ligand).[42] However, the syntheses of **41** and **42** show that, under certain conditions, it is possible to obtain alkylidyne products containing *ortho*-disubstituted imido ligands. Unfortunately, the exact conditions leading to alkylidyne formation are not known at this time.

3.2. X-Ray Crystal Structure of Mo(NH-2,6-$Cl_2C_6H_3$)($CCMe_2Ph$)(*S*-biphen)

The molecular structure of Mo(NH-2,6-$Cl_2C_6H_3$)($CCMe_2Ph$)(*S*-biphen), **42**, was determined by Peter J. Bonitatebus, Jr., by X-ray crystallographic study of single crystals of the complex. Crystallographic data, collection parameters and refinement parameters are given in Table 3.1 while selected bond lengths (Å) and angles (°) are given in Table 3.2. The molecular structure and atom-labeling scheme are shown in Figure 3.1. Yellow crystals of **42** were grown from a mixture of ether and pentane at -30 °C. The complex crystallized in the $P2_12_12_1$ space

group as a four-coordinate, pseudo-tetrahedral molybdenum amido alkylidyne bisaryloxide complex.

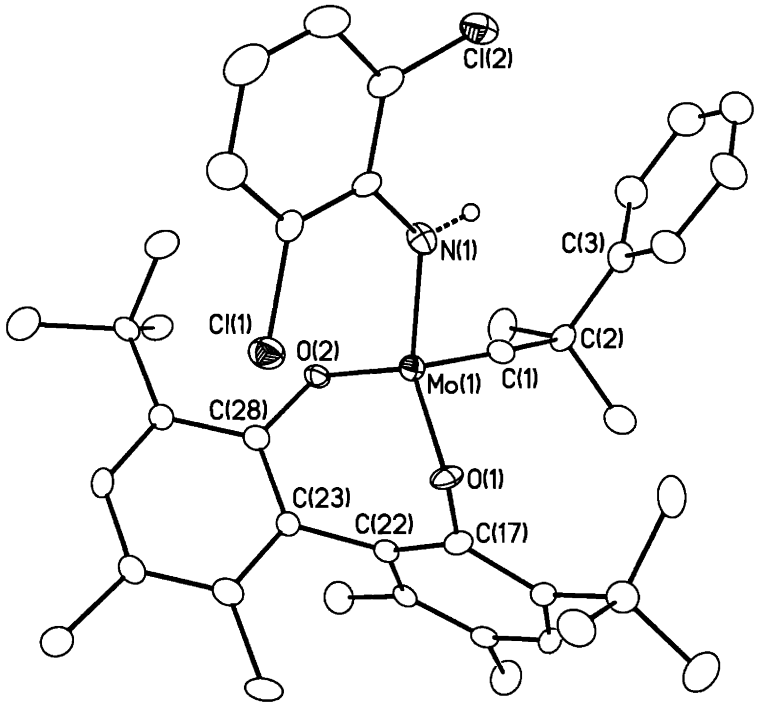


Figure 3.1. ORTEP of Mo(NH-2,6-$Cl_2C_6H_3$)($CCMe_2Ph$)(*S*-biphen), 42.

Table 3.1. Crystallographic Data, Collection Parameters, and Refinement Parameters for Mo(NH-2,6-$Cl_2C_6H_3$)($CCMe_2Ph$)(*S*-biphen) (42).

Empirical formula	$C_{40}H_{47}Cl_2MoNO_2$	
Formula weight	740.63	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	$P2_12_12_1$	
Unit cell dimensions	a = 10.1338(8) Å	α= 90°.
	b = 17.5044(14) Å	β= 90°.
	c = 20.6093(17) Å	γ = 90°.
Volume	3655.8(5) $Å^3$	
Z	4	
Density (calculated)	1.346 Mg/m^3	
Absorption coefficient	0.539 mm^{-1}	
F(000)	1544	
Theta range for data collection	2.24 to 23.31°.	
Index ranges	$-11 \le h \le 11$, $-19 \le k \le 13$, $-22 \le l \le 22$	
Reflections collected	15059	
Independent reflections	5275 (R_{int} = 0.1025)	
Completeness to theta = 23.31°	99.9 %	
Absorption correction	None	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5275 / 0 / 419	
Goodness-of-fit on F^2	0.977	
Final R indices [I>2sigma(I)]	R1 = 0.0559, wR2 = 0.0855	
R indices (all data)	R1 = 0.0877, wR2 = 0.0932	
Absolute structure parameter	0.03(5)	
Largest diff. peak and hole	0.578 and -0.359 $e.Å^{-3}$	

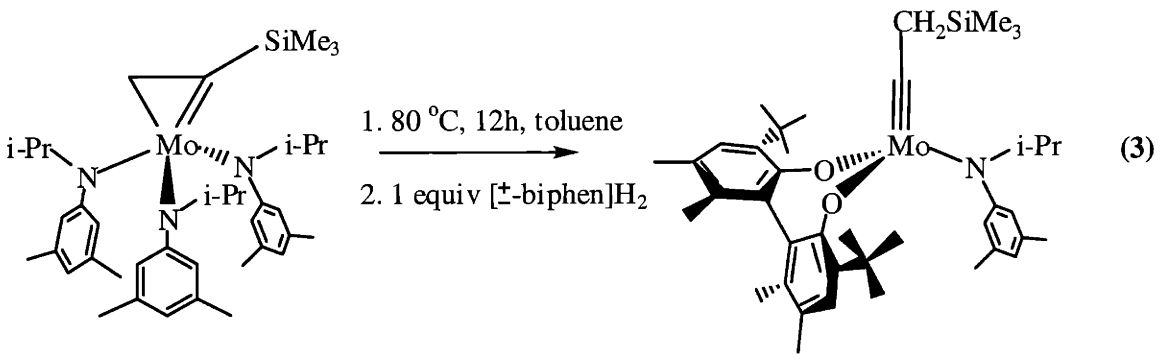
Table 3.2. Selected bond lengths (Å) and angles (°) for Mo(NH-2,6-$Cl_2C_6H_3$)(CCMe_2Ph)(*S*-biphen) (42).

Mo-C(1)	1.721(7)	Mo-N(1)-C_{aryl}	133.8(5)
Mo-O(2)	1.962(4)	Mo-C(1)-C(2)	170.5(5)
Mo-O(1)	1.988(4)	Mo-O(1)-C(17)	98.9(3)
Mo-N(1)	1.990(6)	Mo-O(2)-C(28)	104.6(3)
N(1)-C(11)	1.377(8)		

There are several interesting features to be noted from the X-ray crystal structure of Mo(NH-2,6-$Cl_2C_6H_3$)(CCMe_2Ph)(*S*-biphen), **42**. While it appears that there could be an interaction between the two atoms, the distance between the amido *ortho* chlorine Cl(1) and Mo is too long to be considered a bond (~2.93 Å). As expected, the amido group in complex **42** is more bent (Mo-N-C ~ 134°) than the imido ligand in Mo(N-2,6-$Cl_2C_6H_3$)(C$HCMe_3$)(*S*-biphen)(THF), **16** (Mo=N-C ~ 150°). Also as expected, the alkylidyne group is near-linear (~171°) and the Mo-C distance is shorter than an alkylidene bond length (1.721 Å for **42** compared with 1.872 Å for **16**).

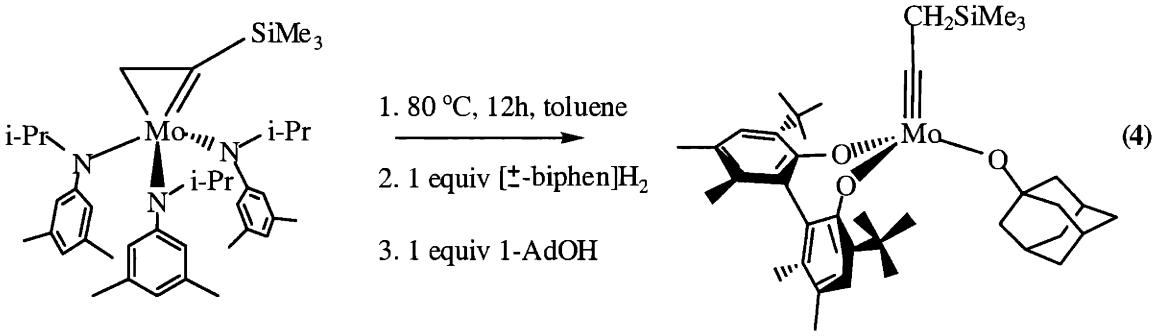
3.3. Synthesis of Molybdenum Alkylidyne Biphen Adamantoxide Complex

Mo(CCH_2SiMe_3)[N(i-Pr)Ar"](±-biphen), **43**, was prepared using methods analogous to the synthesis of Mo(CCH_2SiMe_3)$(OAd)_3$, **40** (Scheme 3.1). Mo(η^2-$H_2CCSiMe_3$)[N(i-Pr)Ar"]$_3$, **38**, was a gift from Yi-Chou Tsai. Complex **38** was heated to 80 °C to give Mo(CCH_2SiMe_3)[N(i-Pr)Ar"]$_3$, **39**, which was then reacted *in situ* with one equiv [±-biphen]H_2 at 80 °C for 15h, giving a mixture of **43** and 2 equiv HN(i-Pr)Ar" (eq 3). Other diols were reacted with **39**, including [*R*-benzhydril]H_2, [±-TRIP]H_2, [*R*-mesitylbinap]H_2 and [±-biphenSiMe_2]H_2, however only [±-biphen]H_2 gave complete conversion to the amido alkylidyne product.



38 **43** (3)

Attempted crystallization and isolation of complex **43** proved difficult as it could not be separated from the HN(i-Pr)Ar" by-product. One equiv 1-adamantanol was reacted *in situ* with the mixture of **43** and HN(i-Pr)Ar" to cleanly generate a mixture of $Mo(CCH_2SiMe_3)(\pm$-biphen)(OAd), **44**, and 3 equiv HN(i-Pr)Ar" (eq 4). Complex **44** was crystallized from cold pentane (-30 °C) to give the product as a beige powder in 46% yield.



38 **44** (4)

The molecular structure of $Mo(CCH_2SiMe_3)(\pm$-biphen)(OAd), **44**, was determined by James P. Araujo by X-ray crystallographic study of single crystals of the complex. Crystallographic data, collection parameters and refinement parameters are given in Table 3.3 while selected bond lengths (Å) and angles (°) are given in Table 3.4. The molecular structure and atom-labeling scheme are shown in Figure 3.2. Pale yellow crystals of **44** were grown from

a concentrated ether and pentane solution at -30 °C. The complex crystallized in the *P*1 space group as a four-coordinate, pseudo-tetrahedral molybdenum alkylidyne biphenoxide adamantoxide complex. Both the *R*- and *S*-biphen containing complexes were present in the unit cell. The alkylidyne bond length is ~1.707 Å and the bond angle is near linear (~168°). The orientation of the $SiMe_3$ group on alkylidyne shows that it is bent away from the adamantoxide group, most likely due to more favorable steric interactions.

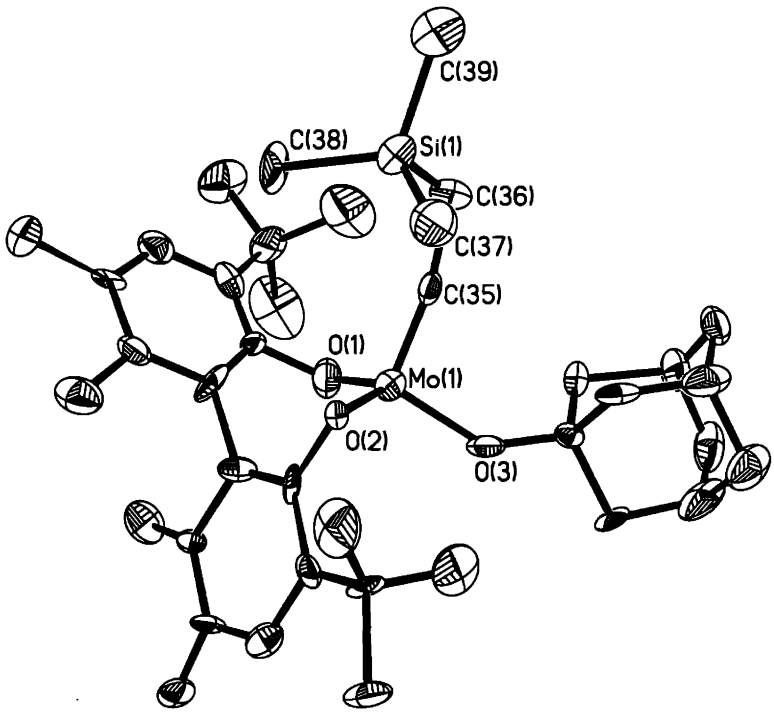


Figure 3.2. ORTEP of Mo(CCH_2SiMe_3)(±-biphen)(OAd), 44.

Table 3.3. Crystallographic Data, Collection Parameters, and Refinement Parameters for $Mo(CCH_2SiMe_3)(\pm\text{-biphen})(OAd)$ (44).

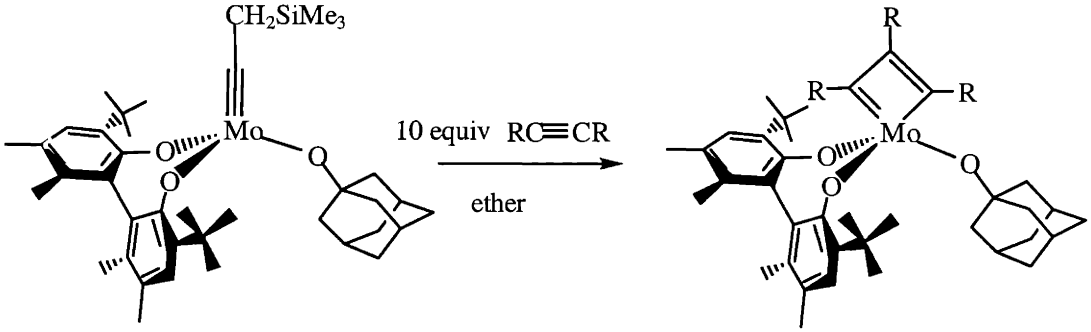
Empirical formula	$MoC_{39}H_{58}O_3Si$	
Formula weight	698.88	
Temperature	183(2) K	
Wavelength	0.71073 Å	
Crystal system, space group	Triclinic, P1	
Unit cell dimensions	a = 10.2512(6) Å	α = 78.5090(10)°
	b = 13.0936(8) Å	β = 76.2910(10)°
	c = 15.9276(10) Å	γ = 85.9270(10)°
Volume	2034.7(2) $Å^3$	
Z, Calculated density	2, 1.141 Mg/m^3	
Absorption coefficient	0.383 mm^{-1}	
F(000)	744	
Theta range for data collection	2.51 to 23.28°	
Limiting indices	$-11 \le h \le 11$, $-9 \le k \le 14$, $-13 \le l \le 17$	
Reflections collected / unique	8181 / 6715 [R_{int} = 0.0445]	
Completeness to theta = 23.29	97.7 %	
Absorption correction	None	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6715 / 3 / 821	
Goodness-of-fit on F^2	1.085	
Final R indices [$I>2\sigma(I)$]	R1 = 0.0663, wR2 = 0.1990	
R indices (all data)	R1 = 0.0696, wR2 = 0.2071	
Absolute structure parameter	0.31(9)	
Largest diff. peak and hole	3.494 and -0.594 $e.A^{-3}$	

Table 3.4. Selected bond lengths (Å) and angles (°) for Mo(CCH_2SiMe_3)(±-biphen)(OAd) (44).

Mo-C(35)	1.707(15)	Mo-C(35)-C(36)	168.3(11)
Mo-O(1)	2.026(10)	Mo-O(1)-C(11)	100.4(8)
Mo-O(2)	1.949(9)	Mo-O(2)-C(17)	101.4(7)
Mo-O(3)	1.858(10)	Mo-O(3)-C(1)	140.2(9)

3.4. Reaction of Mo(CCH_2SiMe_3)(±-biphen)(OAd) with Alkynes

Reaction of Mo(CCH_2SiMe_3)$(OAd)_3$, **40**, with 2-butyne gives Mo(CCH_3)$(OAd)_3$ as a white powder in essentially quantitative yield.[83] Therefore, the expected product of reaction of Mo(CCH_2SiMe_3)(±-biphen)(OAd), **44**, with 10 equiv 2-butyne was Mo(CCH_3)(±-biphen)(OAd). However, instead the reaction mixture immediately turned dark red and the metallacyclobutadiene complex, Mo(C_3Me_3)(±-biphen)(OAd), **45**, was isolated as a rosy red powder in 79% yield (eq 5). Previous molybdacyclobutadiene complexes have been isolated as red or purple solids.[81] The ^1H NMR spectrum (500 MHz, C_6D_6) of **45** was characteristic of a



44 **45** (R = Me)
46 (R = Et)

(5)

metallacyclobutadiene complex with resonances for the two methyl groups attached to the ring α-carbons appearing at 2.89 and 2.74 ppm and a resonance for the β-carbon methyl group at 1.90 ppm. By ^{13}C NMR (125 MHz, C_6D_6), there were three signals corresponding to

metallacyclobutadiene ring carbons at 254.24, 218.03 and 192.79 ppm. Based on characterization of other molybdacyclobutadiene complexes, ^{13}C NMR resonances for C_α typically occur between 200-260 ppm while C_β occur further upfield, between 170-220 ppm.[81]

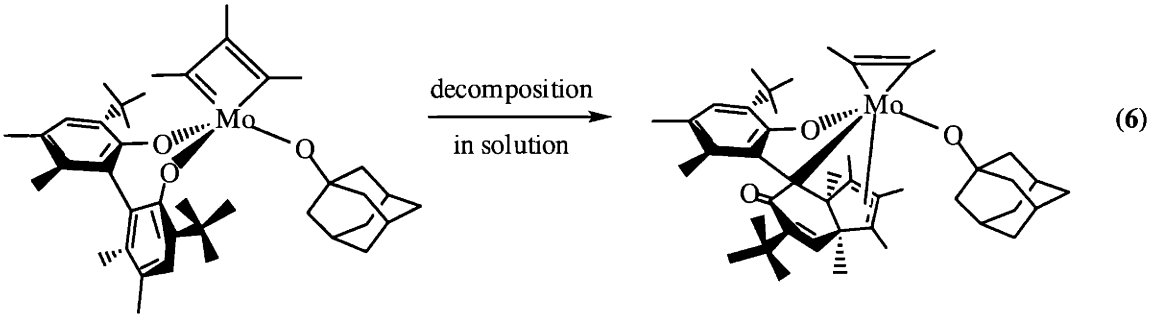
The analogous ethyl-substituted molybdacyclobutadiene complex was synthesized by reaction of **44** with 3-hexyne to give Mo(C_3Et_3)(±-biphen)(OAd), **46**, as a rosy red powder in 59% yield (eq 5). By ^1H NMR (500 MHz, C_6D_6), complex **46** contained three distinct ethyl groups, with the resonances for the four $C_\alpha CH_2$ protons appearing as multiplets at 3.55, 3.04, 2.66 and 1.98 ppm and the resonance for the two $C_\beta CH_2$ protons appearing as a multiplet at 2.94 ppm. Three distinct triplet resonances corresponding to the two $C_\alpha CH_2CH_3$ groups and the $C_\beta CH_2CH_3$ group appeared at 0.64, 0.77 and 1.31 ppm, respectively. It was not possible to confirm the structure of **46** by ^{13}C NMR because it was only sparingly soluble and because it decomposed in solution. Complex **46** was, however, stable over several days in the solid state, allowing for elemental analysis to confirm the chemical composition.

Metallacyclobutadiene complexes have been shown to catalyze the metathesis of alkynes. For example, the tungsten complex W(C_3Me_3)[OCMe(CF_3)$_2$]$_3$ reacts with excess 3-hexyne to give the triethyl metallacyclobutadiene, W(C_3Et_3)[OCMe(CF_3)$_2$]$_3$ within minutes at room temperature.[86] However, Mo(C_3Me_3)(±-biphen)(OAd), **45**, did not react with 20 equiv 3-hexyne to give Mo(C_3Et_3)(±-biphen)(OAd). Complex **45** also showed essentially no reactivity with 3-heptyne after 12h, whereas metallacyclobutadiene complexes W(C_3R_3)[OCMe(CF_3)$_2$]$_3$ (R = Me, Et)[86] and W(C_3R_3)(O-2,6-i-$Pr_2C_6H_3$)$_3$ (R = Et, Pr)[87] catalyze the metathesis of 3-heptyne to give a mixture of 3-hexyne, 3-heptyne and 4-octyne (in a ratio of 1:2:1).

The lack of reactivity of complex **45** is not unique, as there are examples of other metallacyclobutadiene complexes that do *not* catalyze metathesis of alkynes, and instead give cyclopentadienyl complexes.[88] For example, W(C_3Et_3)($OCMe_2CMe_2O$)($OCMe_3$) reacts with 3-hexyne to give W(η^5-C_5Et_5)($OCMe_3$)O_2. A proposed mechanism for this reaction is the insertion of 3-hexyne into an η^3-cyclopropenyl intermediate formed from the metallacyclobutadiene ligand. The reaction of the metallacyclobutadiene complex

$W[C(CMe_3)C(Me)C(Me)]Cl_3$ with TMEDA gave the η^3-cyclopropenyl product, $W[\eta^3\text{-}C_3Me_2(CMe_3)](Me_2NCH_2CH_2NMe_2)Cl_3$, confirming that isomerization of the metallacyclobutadiene fragment can occur.[88]

These previous results are particularly interesting given the observed decomposition of complexes **45** and **46** in solution. Both complexes **45** and **46** are stable over several days in the solid state, however slow decomposition occurs in solution. $Mo(C_3Me_3)$(±-biphen)(OAd), **45**, decomposed to give complex **47** (eq 6), with a structure that was difficult to elucidate from a complicated ^1H NMR spectrum (500 MHz, C_6D_6). The only resonances that could be assigned were for the (±-biphen) backbone: one Ar*H* resonance appeared at 6.85 ppm while the other Ar*H* resonance was shifted far upfield to 5.21 ppm. Only a trace amount of this complex was isolated and the yield varied in different reactions, as determined by ^1H NMR spectroscopy.



45 **47** **(6)**

The molecular structure of Mo(decomp-biphen)(η^2-C_2Me_2)(OAd), **47**, was determined by L. Pia H. Lopez and Paula L. Diaconescu by X-ray crystallographic study of single crystals of the complex. Crystallographic data, collection parameters and refinement parameters are given in Table 3.5 while selected bond lengths (Å) and angles (°) are given in Table 3.6. The molecular structure and atom-labeling scheme are shown in Figure 3.3. Pale yellow crystals of **47** were unexpectedly obtained while attempting to grow crystals of $Mo(C_3Me_3)$(±-biphen)(OAd), **45**, over several days from a concentrated ether and pentane solution at -30 °C. Complex **47** crystallized in the $P\bar{1}$ space group. $Mo(C_3Me_3)$(±-biphen)(OAd), **45**, had

decomposed such that the three-carbon fragment comprising the metallacyclobutadiene moiety had transferred to one ring of the (±-biphen) ligand, forming a bicyclic structure. This three-carbon propenyl fragment was bonded to Mo in an η^3 manner. The Mo-O bond of this distorted half of (±-biphen) had cleaved to give a quinone type structure with a shortened C(17)-O(3) bond length of 1.238(6) Å (compared with C(23)-O(2) = 1.347(6) Å for the remaining coordinated C-O bond). It is thought that the Ar*H* resonance at 5.21 ppm in the ^{1}H NMR spectrum corresponds to the proton on this quinone ring. An additional equiv of 2-butyne was coordinated to molybdenum in an η^2 manner. The geometry of the complex could be best described as a distorted trigonal bipyramid, with the adamantoxide group and C(18) of the distorted (±-biphen) ring occupying the axial positions.

Mo(C_3Et_3)(±-biphen)(OAd), **46**, was stable over several days in the solid state, but slowly decomposed in solution to give a product thought to be analogous to Mo(decomp-biphen)(η^2-C_2Me_2)(OAd), **47**. This is based on the appearance in the ^{1}H NMR spectrum of a signal for a quinone proton at 5.16 ppm. The structure was difficult to elucidate from a complicated ^{1}H NMR spectrum (500 MHz, C_6D_6).

It is possible, based on the formation of tungsten cyclopentadienyl complexes from tungstenacyclobutadiene complexes, that decomposition of both **45** and **46** proceeds via insertion of (±-biphen) into an η^3-cyclopropenyl intermediate.[88] However, the mechanism of this rearrangement is not fully understood at this time.

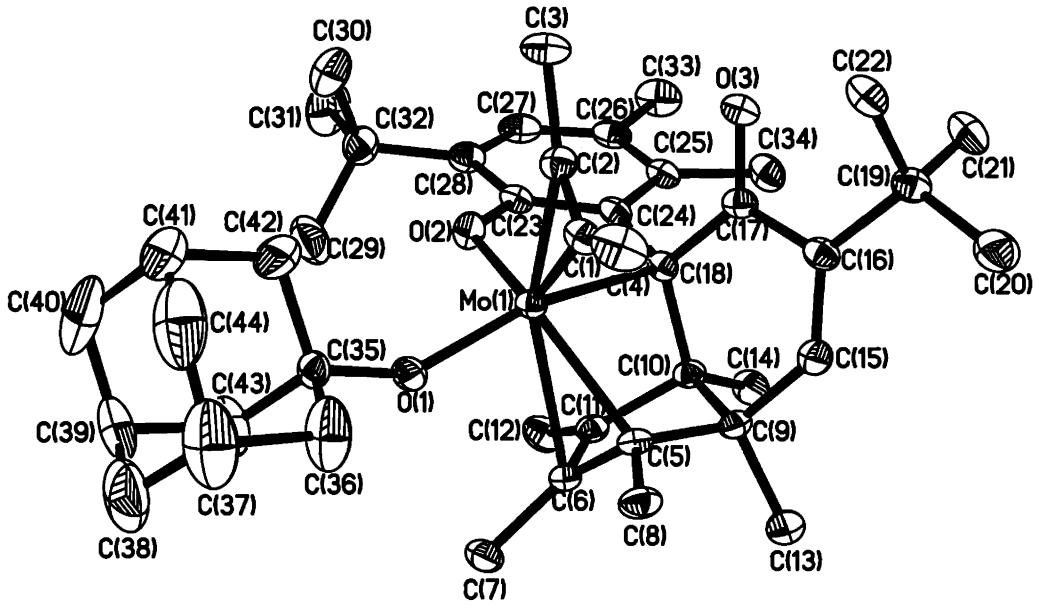


Figure 3.3. ORTEP of decomposition product, Mo(decomp-biphen)(η^2-C_2Me_2)(OAd), 46.

Table 3.5. Crystallographic Data, Collection Parameters, and Refinement Parameters for Mo(decomp-biphen)(η^2-C_2Me_2)(OAd) (46).

Empirical formula	$C_{44}H_{62}MoO_3$	
Formula weight	734.88	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	$P\bar{1}$	
Unit cell dimensions	a = 8.9508(11) Å	α= 78.997(2)°.
	b = 9.9851(12) Å	β= 80.498(2)°.
	c = 22.656(3) Å	γ = 88.923(2)°.
Volume	1960.2(4) $Å^3$	
Z	2	
Density (calculated)	1.245 Mg/m^3	
Absorption coefficient	0.372 mm^{-1}	
F(000)	784	
Theta range for data collection	2.31 to 23.28°.	
Index ranges	$-9 \le h \le 9$, $-6 \le k \le 11$, $-25 \le l \le 25$	
Reflections collected	8002	
Independent reflections	5534 [R_{int} = 0.0604]	
Completeness to theta = 23.28°	98.3 %	
Absorption correction	None	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5534 / 0 / 449	
Goodness-of-fit on F^2	1.059	
Final R indices [I>2sigma(I)]	R1 = 0.0565, wR2 = 0.1240	
R indices (all data)	R1 = 0.0690, wR2 = 0.1300	
Extinction coefficient	0.0000(5)	
Largest diff. peak and hole	0.532 and -0.721 $e.Å^{-3}$	

Table 3.6. Selected bond lengths (Å) and angles (°) for Mo(decomp-biphen)(η^2-C_2Me_2)(OAd) (46).

Mo-O(1)	1.873(3)	O(1)-Mo-C(18)	155.76(15)
Mo-O(2)	1.996(3)	O(1)-Mo-O(2)	96.57(14)
Mo-C(1)	2.013(5)	O(1)-Mo-C(5)	95.57(16)
Mo-C(2)	1.999(5)	O(1)-Mo-C(1)	101.21(17)
Mo-C(5)	2.226(5)	C(18)-Mo-O(2)	74.59(15)
Mo-C(6)	2.488(5)	C(18)-Mo-C(5)	77.47(17)
Mo-C(18)	2.389(4)	C(18)-Mo-C(1)	102.29(17)
C(23)-O(2)	1.347(6)	O(2)-Mo-C(1)	124.93(18)
C(17)-O(3)	1.238(6)	O(2)-Mo-C(5)	136.73(16)
C(10)-C(11)	1.542(7)	C(2)-Mo-C(5)	123.5(2)
C(6)-C(11)	1.367(7)		
C(5)-C(6)	1.490(7)		
C(5)-C(9)	1.539(7)		
C(1)-C(2)	1.307(7)	C(1)-C(2)-C(3)	145.4(5)
C(1)-C(4)	1.498(7)	C(2)-C(1)-C(4)	140.3(5)
C(2)-C(3)	1.475(7)		

comparison of distorted biphen ring and normal ring:

C(15)-C(16)	1.333(7)	C(27)-C(28)	1.394(7)
C(10)-C(18)	1.544(6)	C(24)-C(25)	1.418(7)
C(9)-C(10)	1.550(7)	C(25)-C(26)	1.405(7)
C(16)-C(17)-C(18)	118.9(4)	C(24)-C(23)-C(28)	122.7(5)
C(10)-C(9)-C(15)	113.1(4)	C(25)-C(26)-C(27)	119.9(5)

CONCLUSIONS

In rare cases, reaction of deprotonated [biphen]H_2 with a molybdenum imido alkylidene bistriflate complex produces an amido alkylidyne product. For example, in two isolated reactions, Mo(NH-2,6-$Cl_2C_6H_3$)($CCMe_3$)(±-biphen) (**41**) and Mo(NH-2,6-$Cl_2C_6H_3$)($CCMe_2Ph$)(*S*-biphen) (**42**) were produced. The structure of **42** was confirmed by X-ray crystallography. However, all attempts to reproduce conditions leading to alkylidyne formation were unsuccessful. A more reproducible synthesis of a molybdenum alkylidyne complex was the synthesis of Mo(CCH_2SiMe_3)(±-biphen)(OAd) (**44**) by stepwise addition of [±-biphen]H_2 and 1-AdOH to Mo(CCH_2SiMe_3)[N(i-Pr)Ar"]$_3$. Complex **44** reacted with 2-butyne and 3-hexyne to give metallacyclobutadiene complexes, Mo(C_3Me_3)(±-biphen)(OAd) (**45**) and Mo(C_3Et_3)(±-biphen)(OAd) (**46**). Complexes **45** and **46** were stable in the solid state and **45** did not catalyze the metathesis of alkynes. Both complexes appeared to decompose slowly in solution to give an unusual structure in which the metallacyclobutadiene fragment had transferred to the (±-biphen) ring. The structure of this decomposition product was determined by X-ray crystallography.

EXPERIMENTAL

General Details. All experiments were conducted under nitrogen in a Vacuum Atmospheres drybox or using standard Schlenk techniques. THF, toluene, ether, and pentane were sparged with nitrogen and passed through alumina columns. Benzene was distilled from sodium benzophenone ketyl. Benzyl potassium,[66] [±-biphen]H_2,[40] [*S*-biphen]H_2,[42] Mo(N-2,6-$Cl_2C_6H_3$)($CHCMe_3$)($OTf)_2$(dme) (**14**),[47] and Mo(N-2,6-$Cl_2C_6H_3$)($CHCMe_2Ph$)($OTf)_2(THF)_x$ (**15**) were prepared by reported methods. Mo(η^2-CH_2CSiMe_3)[N(i-Pr)Ar"]$_3$ (**38**) was a gift from Y.-C. Tsai.[83] [±-Biphen]H_2 and [*S*-biphen]H_2 were gifts from John B. Alexander. 1-Adamantanol was used as received from Aldrich. 2-Butyne and 3-hexyne were filtered through alumina before use. C_6D_6 and toluene-d_8 were sparged with nitrogen and stored over 4 Å molecular sieves. ^1H and ^{13}C NMR data are listed in parts per million downfield from

tetramethylsilane and were referenced using the residual protio solvent resonance. Routine NMR coupling constants are not reported. Spectra were obtained at room temperature. Elemental analyses were performed by H. Kolbe Laboratories, Mülheim an der Ruhr, Germany.

Mo(NH-2,6-$Cl_2C_6H_3$)($CCMe_3$)(±-biphen) (41)

Benzyl potassium (96 mg, 0.58 mmol) was added to [±-biphen]H_2 (104 mg, 0.29 mmol) in THF (2 mL). Mo(N-2,6-$Cl_2C_6H_3$)($CHCMe_3$)$(OTf)_2$(dme) (200 mg, 0.29 mmol) was then added, turning the mixture dark red. After 24h, the solvent was evaporated and the residue suspended in benzene and filtered through Celite. The benzene was evaporated and the residue was dissolved in ether and stored at -30 °C to give the product as a yellow powder after 1 month (32 mg, 16.8%). ^{1}H NMR (500 MHz, C_6D_6): 11.73 (s, 1, N*H*), 7.40 (s, 1, Ar*H*), 7.25 (s, 1, Ar*H*), 6.69 (br s, 2, Ar*H*), 6.05 (t, 1, Ar*H*), 2.20 (s, 3, ArCH_3), 2.17 (s, 3, ArCH_3), 1.75 (s, 3 + 9, ArCH_3 + ArC(CH_3)$_3$), 1.67 (s, 3, ArCH_3), 1.39 (s, 9, ArC(CH_3)$_3$), 1.01 (s, 9, Mo≡CC(CH_3)$_3$). ^{13}C NMR (125 MHz, C_6D_6): 327.74, 160.63, 155.81, 147.20, 137.15, 135.74, 135.06, 131.16, 130.34, 129.91, 129.75, 129.69, 128.67, 128.32, 127.70, 121.42, 54.96, 36.12, 35.63, 30.97, 30.22, 28.84, 20.89, 20.85, 17.18, 17.03. Anal. Calcd. for $MoC_{35}H_{45}Cl_2NO_2$: C 61.95, H 6.68, N 2.06, Cl 10.45; Found: C 62.08, H 6.75, N 1.98, Cl 10.31.

Mo(NH-2,6-$Cl_2C_6H_3$)($CCMe_2Ph$)(*S*-biphen) (42)

Benzyl potassium (151 mg, 1.16 mmol) in THF (2 mL) was added to [*S*-biphen]H_2 (187 mg, 0.53 mmol) in THF (2 mL) until endpoint. After stirring 10 min, the mixture was added dropwise to a suspension of Mo(N-2,6-$Cl_2C_6H_3$)($CHCMe_2Ph$)$(OTf)_2(THF)_x$ (400 mg, 0.53 mmol) in THF (5 mL). The mixture turned dark red and homogeneous. After stirring for 20h, the solvent was evaporated and the residue suspended in toluene, filtered through Celite and evaporated to give a red oil. The red oil was dissolved in ether (2 mL) and stored at –30 °C to give Mo(NH-2,6-$Cl_2C_6H_3$)($CCMe_2Ph$)(*S*-biphen) as a yellow powder that was isolated by filtration (147 mg, 37.5 %). ^{1}H NMR (500 MHz, C_6D_6): 11.59 (s, 1, N*H*), 7.45 (d, 2, Ar*H*), 7.33

(s, 1, Ar*H*), 7.26 (s, 1, Ar*H*), 7.21 (t, 2, Ar*H*), 7.09 (t, 1, Ar*H*), 6.66 (br s, 2, Ar*H*), 6.03 (t, 1, Ar*H*), 2.20 (s, 3, ArCH_3), 2.17 (s, 3, ArCH_3), 1.78 (s, 3, ArCH_3), 1.67 (s, 3, ArCH_3), 1.65 (s, 9, C(CH_3)$_3$), 1.45 (s, 3, C(CH_3)$_2$Ph), 1.38 (s, 9 + 3, C(CH_3)$_3$ + C(CH_3)$_2$Ph). ^{13}C NMR (125 MHz, C_6D_6): 322.13, 160.68, 155.92, 147.21, 146.31, 137.36, 137.17, 135.67, 135.13, 131.37, 130.38, 129.99, 129.88, 129.74, 129.17, 127.62, 126.88, 126.82, 121.48, 61.77, 36.06, 35.62, 30.86, 30.21, 29.59, 28.79, 20.91, 17.20, 17.05. Anal. Calcd. for $MoC_{40}H_{47}NCl_2O_2$: C 64.87, H 6.40, N 1.89, Cl 9.57; Found: C 64.75, H 6.48, N 1.77, Cl 9.71.

Mo(CCH$_2$SiMe$_3$)(±-biphen)(OAd) (44)

Mo(η^2-CH$_2$CSiMe$_3$)[N(i-Pr)Ar"]$_3$ (2.00 g, 2.93 mmol) was dissolved in toluene (60 mL) and heated to 80 °C in a Teflon-sealed Schlenk flask until complete conversion to the alkylidyne was observed by ^{1}H NMR (~18h). The reaction mixture was then cooled to room temperature and [±-biphen]H$_2$ (1.04 g, 2.93 mmol) was added. The solution was heated to 80 °C, until complete conversion to Mo(CCH$_2$SiMe$_3$)[N(i-Pr)Ar"](±-biphen), **43**, was observed by ^{1}H NMR (18-48h). The ^{1}H NMR spectrum (500 MHz, toluene-d_8) of the mixture of Mo(CCH$_2$SiMe$_3$)[N(i-Pr)Ar"](±-biphen) and 2 equiv HN(i-Pr)Ar" is assigned as follows: Mo(CCH$_2$SiMe$_3$)[N(i-Pr)Ar"](±-biphen): 7.29 (s, 1, Ar*H*), 6.73 (s, 1, Ar*H*), 6.34 (s, 1, *para* Ar*H* amido), 6.30 (s, 2, *ortho* Ar*H* amido), 4.28 (sept, 1, C*H*Me$_2$), 2.85 (s, 2, MoCCH_2), 2.17 (s, 3, ArCH_3 biphen), 2.03 (s, 3, ArCH_3 biphen),1.94 (s, 6, ArCH_3 amido), 1.73 (s, 9, C(CH_3)$_3$), 1.69 (s, 3, ArCH_3 biphen),1.63 (d, 6, CH(CH_3)$_2$),1.56 (s, 3, ArCH_3 biphen), 1.20 (s, 9, C(CH_3)$_3$), -0.02 (s, 9, Si(CH_3)$_3$). 2 equiv HN(i-Pr)Ar": 6.59 (s, 2, *para* Ar*H*), 6.05 (s, 4, *ortho* Ar*H*), 3.37-3.31 (m, 2, C*H*Me$_2$), 2.85 (br s, 2, N*H*), 2.16 (s, 12, ArCH_3), 0.92 (d, 12, CH(CH_3)$_2$). The solution was cooled to room temperature and 1-adamantanol (0.44 g, 2.93 mmol) in THF (15 mL) was added. The reaction was stirred at room temperature (~24h) until complete conversion to the desired product was determined by ^{1}H NMR. The solvent was evaporated and the resulting residue dissolved in minimal pentane and stored at -30 °C for 12h. The product, Mo(CCH$_2$SiMe$_3$)(±-biphen)(OAd), was isolated by filtration as a beige crystalline solid (0.95 g, 46.2%). ^{1}H NMR

(500 MHz, C_6D_6): 7.39 (s, 1, Ar*H*), 7.15 (s, 1, Ar*H*), 2.98 (m, 3, Ad), 2.20 (s, 3, ArCH_3), 2.08 (s, 6 + 2, Ad + MoCCH_2), 1.94 (s, 3, ArCH_3), 1.82 (s, 9, C(CH_3)$_3$), 1.74 (s, 3, ArCH_3), 1.63 (s, 3, ArCH_3), 1.61 (s, 9, C(CH_3)$_3$), 1.54-1.51 (m, 6, Ad), 0.04 (s, 9, Si(CH_3)$_3$). ^{13}C NMR (125 MHz, C_6D_6): 307.76, 155.58, 149.56, 140.52, 139.25, 135.88, 135.29, 131.32, 131.04, 130.69, 129.85, 129.66, 127.19, 82.58, 47.75, 47.57, 36.87, 36.25, 35.48, 32.11, 30.81, 30.77, 20.92, 20.63, 16.98, 16.68, -0.85. Anal. Calcd. for $MoC_{39}H_{58}SiO_3$: C 67.02, H 8.36; Found: C 67.15, H 8.31.

Mo(C_3Me_3)(±-biphen)(OAd) (45)

2-Butyne (193 mg, 3.58 mmol) was added to Mo(CCH_2SiMe_3)(±-biphen)(OAd) (**44**) (250 mg, 0.36 mmol) in ether (2 mL) and the colorless solution immediately turned dark red. After stirring for 12h, Mo(C_3Me_3)(±-biphen)(OAd) was isolated by filtration as a rosy-red powder (192 mg, 78.7%). ^{1}H NMR (500 MHz, C_6D_6): 7.21 (s, 1, Ar*H*), 6.09 (s, 1, Ar*H*), 2.89 (br s, 3, α–C_3CH_3), 2.74 (br s, 3, α–C_3CH_3), 2.26 (s, 3, ArCH_3), 2.01 (s, 3, ArCH_3), 1.90 (s, 3, β–C_3CH_3), 1.88 (s, 3, ArCH_3), 1.86 (s, 3, ArCH_3), 1.72 (s, 9, C(CH_3)$_3$), 1.43 (s, 9, C(CH_3)$_3$), 1.41 (m, 9, OAd), 0.80 (s, 3, OAd), 0.67 (s, 3, OAd). ^{13}C NMR (125 MHz, C_6D_6): 254.24, 218.03, 192.79, 169.26, 163.98, 144.85, 139.94, 137.87, 135.65, 134.16, 126.67, 125.92, 120.10, 90.48, 82.08, 64.45, 63.94, 47.04, 36.56, 35.17, 35.10, 31.73, 30.45, 30.41, 23.17, 22.22, 21.80, 21.15, 19.75, 18.09, 17.24, 15.39, 14.46. Anal. Calcd. for $MoC_{40}H_{56}O_3$: C 70.57, H 8.29; Found: C 70.46, H 8.25.

Mo(C_3Et_3)(±-biphen)(OAd) (46)

3-Hexyne (235 mg, 2.86 mmol) was added to Mo(CCH_2SiMe_3)(±-biphen)(OAd) (**44**) (200 mg, 0.29 mmol) in ether (2 mL) and the solution immediately turned from colorless to dark red. After stirring for 12h, Mo(C_3Et_3)(±-biphen)(OAd), **47**, was isolated by filtration as a rosy-red powder (122 mg, 59.0%). ^{1}H NMR (500 MHz, C_6D_6): 7.22 (s, 1, Ar*H*), 6.45 (s, 1, Ar*H*), 3.57-3.52 (m, 1, α–C_3CH_2), 3.07-3.00 (m, 1, α–C_3CH_2), 2.98-2.90 (m, 2, β–C_3CH_2), 2.68-2.62 (m, 1, α–C_3CH_2), 2.26 (s, 3, ArCH_3), 2.11 (s, 3, ArCH_3), 2.02-1.96 (m, 1, α–C_3CH_3), 1.78 (s, 3 + 9,

ArCH_3 + C(CH_3)$_3$), 1.73 (s, 3, ArCH_3), 1.73-1.69 (m, 3, OAd), 1.66 (s, 9, C(CH_3)$_3$), 1.31 (t, 3, β–$C_3CH_2CH_3$), 1.32-1.23 (m, 6, OAd), 0.93 (d, 6, OAd), 0.77 (t, 3, α–$C_3CH_2CH_3$), 0.64 (t, 3, α–$C_3CH_2CH_3$). Anal. Calcd. for $MoC_{43}H_{62}O_3$: C 71.44, H 8.64; Found: C 71.60, H 8.56.

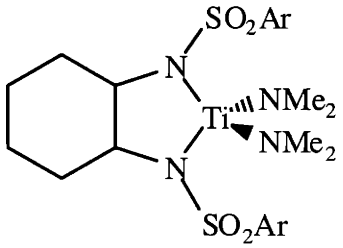
Appendix A

SYNTHESIS OF ZIRCONIUM COMPLEXES CONTAINING N,N'-DISUBSTITUTED-2,2'-DIAMINO-1,1'-BINAPHTHYL LIGANDS

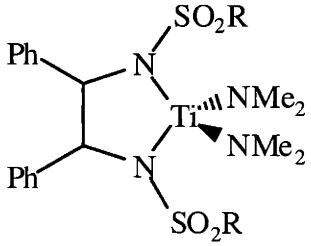
INTRODUCTION

The utility of chelating diamido ligands in stabilizing group 4 single site polymerization catalysts has been well-documented.[85,89] Work presented in Chapter 2 showed that molybdenum imido alkylidene complexes containing the ligand 2,2'-bis-*p*-tolylsulfonamido-1,1'-binaphthyl, [BINA(NTs_2)], were unreactive towards olefin substrates.[90] The X-ray crystal structure of Mo(N-2-$CF_3C_6H_4$)($CHCMe_3$)[BINA(NTs_2)] (Figure 2.2) showed that one sulfonyl group was coordinated to molybdenum. This led us to consider applications of this ligand in the stabilization of group 4 single site polymerization catalysts. The goal of this project was to study zirconium dialkyl complexes of [BINA(NTs_2)].

Bis(sulfonamido) complexes of titanium have been previously synthesized, however the olefin polymerization reactions of these species have not been reported. These complexes include [1,2-(NSO_2Ar)cyclohexyl]Ti(NMe_2)$_2$ (**A-1**, Ar = C_6H_5, 4-MeC_6H_4, 2,4,6-$Me_3C_6H_2$, 2,4,6-i-$Pr_3C_6H_2$),[77,78] and [$N(SO_2R)CHPhCHPhN(SO_2R)$]Ti(NMe_2)$_2$ (**A-2**, R = 4-MeC_6H_4, 4-t-BuC_6H_4, CF_3).[79] X-ray crystallographic study of these complexes showed that there was coordination of a sulfonyl group to titanium.



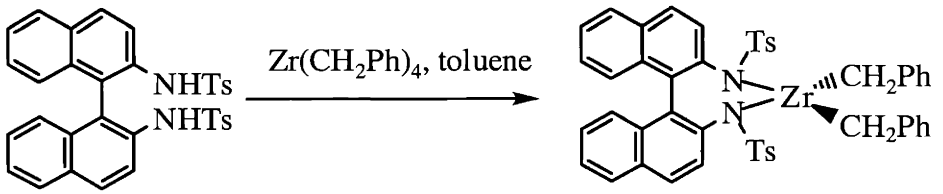
A-1



A-2

RESULTS AND DISCUSSION

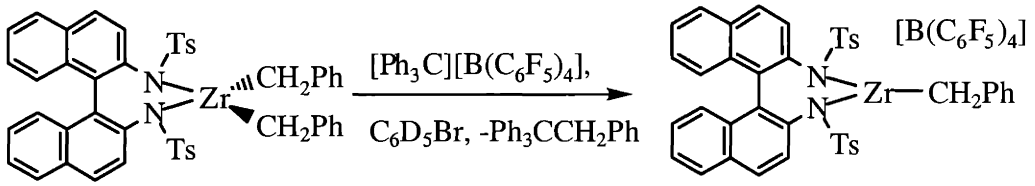
Reaction of [BINA(NTs_2)]H_2 (**30**) with $Zr(CH_2Ph)_4$ in toluene afforded the dibenzyl complex, [BINA(NTs_2)]Zr(CH_2Ph)$_2$ (**A-3**) as a yellow powder in essentially quantitative yield (eq 1).



(1)

30 **A-3**

Activation of **A-3** with $[Ph_3C][B(C_6F_5)_4]$ in bromobenzene-d^5 cleanly produced $\{[BINA(NTs)_2]Zr(CH_2Ph)\}[B(C_6F_5)_4]$ (**A-4**) and Ph_3CCH_2Ph, as a homogeneous yellow solution in bromobenzene-d^5 (eq 2). By ^1H NMR (500 MHz, C_6D_5Br), **A-4** was produced in



(2)

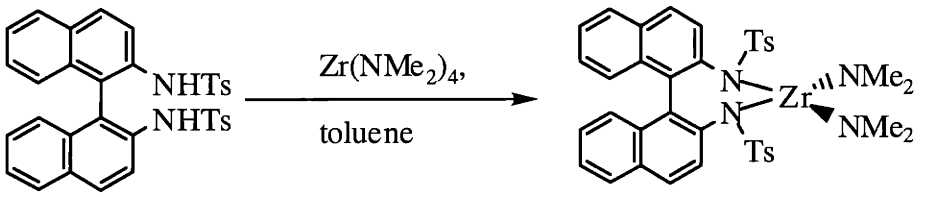
A-3 **A-4**

quantitative yield. Two doublet resonances occurred at 3.82 and 2.74 ppm, one for each benzyl $ZrCH_2$ proton. There was also an increase in the number of aromatic proton resonances due to the loss of symmetry in the molecule, rendering the two halves of the $[BINA(NTs)_2]$ ligand inequivalent. Two singlets corresponding to the methyl groups of the inequivalent tosyl substituents were observed at 1.82 and 1.80 ppm. After 48h at room temperature, there was no significant change in the spectrum of this complex, indicating that it was stable in solution under these conditions. **A-4** was also stable when heated to 80 °C.

Addition of 20 equiv of 1-hexene to **A-4** in C_6D_5Br turned the mixture cloudy after 15 min. After 14h, however, the ^1H NMR spectrum (500 MHz) showed mainly unreacted 1-hexene. In another reaction, **A-4** was reacted with 20 equiv of 1-hexene at 60 °C in a sealed NMR tube. After 17h, the color of the solution had not changed and a thick pellet of yellow-

white precipitate had formed. The mixture was cooled to room temperature and the ^1H NMR spectrum (500 MHz, C_6D_5Br) showed only a trace of 1-hexene and broad resonances corresponding to oligomeric materials.

Reaction of $[BINA(NTs)_2]H_2$ with 1.5 equiv $Zr(NMe_2)_4$ gave $[BINA(NTs)_2]Zr(NMe_2)_2$ (**A-5**) as a white powder in quantitative yield (eq 3). A slight excess of $Zr(NMe_2)_4$ was used to prevent the formation of trace amounts of $[BINA(NTs)_2]_2Zr$. Unreacted $Zr(NMe_2)_4$ was separated from **A-5** by washing with pentane.



30 **A-5** (3)

Reaction of $ClSiMe_3$ with **A-5** did not cleanly generate $[BINA(NTs)_2]ZrCl_2$. The ^1H NMR spectrum (500 MHz, C_6D_6) of the resulting white powder showed that the NMe_2 groups had reacted and that a new $[BINA(NTs)_2]$ complex had been synthesized. There were trace impurities, including new $[BINA(NTs)_2]$ resonances and these could not be separated from the major product.

Attempted syntheses of Zr complexes of $[BINA(N\text{-}i\text{-}Pr)_2]H_2$ (**36**) were unsuccessful. $[BINA(N\text{-}i\text{-}Pr)_2]H_2$ did not react with $Zr(CH_2Ph)_4$ in toluene at room temperature or at 60 °C. Reaction of $Zr(NMe_2)_4$ with $[BINA(N\text{-}i\text{-}Pr)_2]H_2$ in toluene at room temperature showed only 20% conversion to the desired $[BINA(N\text{-}i\text{-}Pr)_2]Zr(NMe_2)_2$ after 24h. At 60 °C, the reaction reached 50% conversion to the desired product within 17h however no further reaction was detected, even after 60h.

Similar problems were encountered in the attempted syntheses of Zr complexes of

$[BINA(NTMS)_2]H_2$ (**34**). $Zr(CH_2Ph)_4$ did not react with $[BINA(NTMS)_2]H_2$ in toluene or THF after 24h at room temperature. No reaction was observed between $[BINA(NTMS)_2]H_2$ and $Zr(NMe_2)_4$ at room temperature in toluene after 22h. When heated to 60 °C, the reaction of $[BINA(NTMS)_2]H_2$ and $Zr(NMe_2)_4$ progressed slowly, leading to 66% conversion after 8 days.

EXPERIMENTAL

General Details. All experiments were conducted under nitrogen in a Vacuum Atmospheres drybox or using standard Schlenk techniques. THF, toluene, diethyl ether, and pentane were sparged with nitrogen and passed through alumina columns. $[BINA(NTs)_2]H_2$ (**30**),[90] $Zr(CH_2Ph)_4$,[91] and $Zr(NMe_2)_4$,[92] were prepared according to literature procedures. $Zr(CH_2Ph)_4$ and $Zr(NMe_2)_4$ were gifts from Denyce K. Wicht. $[Ph_3C][B(C_6F_5)_4]$ was a gift from the Exxon Chemical Corporation. All other reagents were used as received from commercial sources. C_6D_5Br and C_6D_6 were sparged with nitrogen and stored over 4 Å molecular sieves. ^1H and ^{13}C NMR data are listed in parts per million downfield from tetramethylsilane and were referenced using the residual protio solvent resonance. Routine NMR coupling constants are not reported. Spectra were obtained at room temperature. Elemental analyses were performed by H. Kolbe Laboratories, Mülheim an der Ruhr, Germany.

$[BINA(NTs)_2]Zr(CH_2Ph)_2$ (A-3)

$[BINA(NTs)_2]H_2$ (40 mg, 0.067 mmol) was suspended in a toluene (3 mL) solution of $Zr(CH_2Ph)_4$ (30 mg, 0.067 mmol) and stirred for 12h at room temperature. The resulting yellow precipitate was isolated by filtration to give $[BINA(NTs)_2]Zr(CH_2Ph)_2$ (58 mg, 100%). ^1H NMR (C_6D_6, 500 MHz): 8.12 (d, 2, Ar*H*), 7.61 (d, 2, Ar*H*), 7.44 (d, 2, Ar*H*), 7.38 (d, 4, Ar*H*), 7.10 (t, 4, Ar*H*), 6.90 (m, 8, Ar*H*), 6.40 (d, 4, Ar*H*), 5.90 (d, 4, Ar*H*), 2.63 (dd, 4, CH_2Ph), 1.47 (s, 6, ArCH_3). ^{13}C NMR (C_6D_6, 125 MHz): 143.54, 140.89, 138.08, 135.43, 134.74, 132.34, 131.17, 130.08, 129.39, 129.35, 129.10, 127.88, 127.70, 127.41, 126.22, 126.18, 125.33, 124.36, 68.75, 21.17. Anal. Calcd. for $ZrC_{48}H_{40}N_2S_2O_4$: C 66.71, H 4.67, N 3.24; Found: C 66.49, H

4.74, N 3.16.

^{1}H NMR detection of {[BINA(NTs)$_2$]Zr(CH$_2$Ph)}[B(C$_6$F$_5$)$_4$] (A-4)

[BINA(NTs)$_2$]Zr(CH$_2$Ph)$_2$ (19 mg, 0.022 mmol) and [Ph$_3$C][B(C$_6$F$_5$)$_4$] (20 mg, 0.022 mmol) were combined in C$_6$D$_5$Br in a NMR tube at room temperature. After 10 min, the ^{1}H NMR spectrum was obtained. ^{1}H NMR (500 MHz, C$_6$D$_5$Br): 8.03 (d, 1, Ar*H*), 7.98 (d, 1, Ar*H*), 7.73 (d, 1, Ar*H*), 7.58 (d, 1, Ar*H*), 7.32 (d, 1, Ar*H*), 7.30 (d, 1, Ar*H*), 7.11 (d, 8, Ar*H*), 7.01 (t, 8, Ar*H*), 6.95 (d, 4, Ar*H*), 6.88 (t, 3, Ar*H*), 6.80 (t, 3, Ar*H*), 6.70 (d, 1, Ar*H*), 6.66 (d, 1, Ar*H*), 6.57 (t, 5, Ar*H*), 6.45 (t, 1, Ar*H*), 6.40 (d, 1, Ar*H*), 6.36 (d, 2, Ar*H*), 6.26 (t, 1, Ar*H*), 6.22 (d, 2, Ar*H*), 5.76 (d, 1, Ar*H*), 3.82 (d, 1, C*H*$_2$Ph), 3.75 (s, 2, Ph$_3$CC*H*$_2$Ph), 2.74 (d, 1, C*H*$_2$Ph), 2.09 (s, 1, toluene), 1.82 (s, 3, ArC*H*$_3$), 1.80 (s, 3, ArC*H*$_3$).

[BINA(NTs)$_2$]Zr(NMe$_2$)$_2$ (A-5)

[BINA(NTs)$_2$]H$_2$ (100 mg, 0.17 mmol) was added as a solid to Zr(NMe$_2$)$_4$ (68 mg, 0.25 mmol) in toluene (10 mL). The mixture was stirred for 16h, the solvent evaporated and the residue rinsed with pentane. The resulting white solid was dried *in vacuo* to give [BINA(NTs)$_2$]Zr(NMe$_2$)$_2$ (134 mg, 100%). ^{1}H NMR (C$_6$D$_6$, 500 MHz): 8.27 (d, 2, Ar*H*), 7.67 (d, 2, Ar*H*), 7.47 (d, 2, Ar*H*), 7.14 (d, 4, Ar*H*), 6.93 (t, 2, Ar*H*), 6.51 (d, 2, Ar*H*), 6.45 (t, 2, Ar*H*), 5.96 (d, 4, Ar*H*), 3.31 (s, 12, N(C*H*$_3$)$_2$), 1.52 (s, 6, ArC*H*$_3$). ^{13}C NMR (C$_6$D$_6$, 125 MHz): 142.83, 138.23, 137.45, 135.06, 132.23, 130.29, 129.48, 129.29, 128.04, 127.89, 127.05, 126.65, 126.23, 125.07, 42.56, 21.19. Anal. Calcd. for ZrC$_{40}$H$_{38}$N$_4$S$_2$O$_4$: C 60.50, H 4.82, N 7.06; Found: C 60.37, H 4.74, N 6.98.

^{1}H NMR Detection of [BINA(NTs)$_2$]ZrCl$_2$

ClSiMe$_3$ (341 mg, 3.14 mmol) was added via syringe to a suspension of [BINA(NTs)$_2$]Zr(NMe$_2$)$_2$ (250 mg, 0.31 mmol) in ether (5 mL) and stirred for 46h. The white suspension was then evaporated to dryness to give a white residue that was washed with pentane

and dried *in vacuo*. ^{1}H NMR (C_6D_6, 500 MHz): (major product) 8.87 (d, 2, Ar*H*), 7.80 (d, 2, Ar*H*), 7.55 (d, 2, Ar*H*), 7.50 (d, 4, Ar*H*), 7.00 (t, 2, Ar*H*), 6.83 (d, 2, Ar*H*), 6.59 (t, 2, Ar*H*), 6.08 (d, 4, Ar*H*), 1.48 (s, 6, ArCH_3).

Appendix B

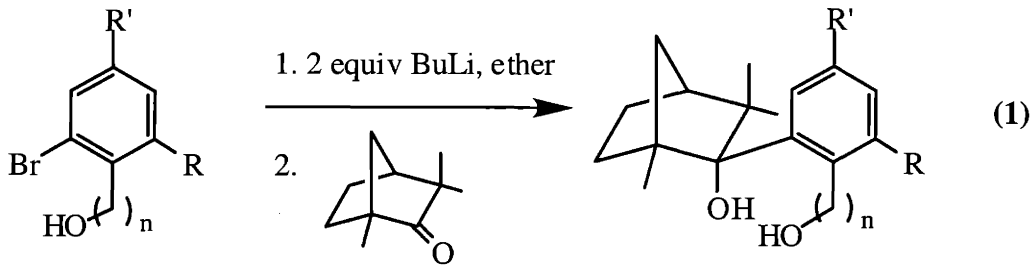
SYNTHESIS OF C_1-SYMMETRIC DIOLS

INTRODUCTION

Molybdenum imido alkylidene complexes containing optically pure, C_2-symmetric bisaryloxide ligands have been shown to catalyze the asymmetric ring-closing metathesis of olefins.[35] In order to obtain these diols in their optically pure form, the racemic mixture must be resolved. The synthesis of C_1-symmetric diols would provide optically pure ligands without such resolution procedures.

RESULTS AND DISCUSSION

The general procedure for the synthesis of C_1-symmetric diols (eq 1) was to react one equiv of an *ortho*-bromophenol with 2 equiv butyllithium. The resulting lithiated phenoxide then reacted with *R*-fenchone exclusively via nucleophilic addition of the lithiated carbon, rather than oxygen.[93,94] Acidic workup gave the 2-fencholphenol compounds, diols **B-1**, **B-2** and **B-3**, all as white powders. Fenchone was used because nucleophilic addition at the carbonyl gives the *endo*-alcohol exclusively[95] and because it contains no enolizable protons. Syntheses of analogous diols using camphor were unsuccessful due to abstraction of the enolizable protons by lithiated phenol. Deprotonation of these diols with benzyl potassium followed by treatment with Mo(N-2,6-i-$Pr_2C_6H_3$)(CHCMe$_2$Ph)(OTf)$_2$(dme)[16] did not yield the corresponding molybdenum imido alkylidene bisalkoxide complexes.



(1)

B-1 (R = R' = H; n = 0)
B-2 (R = R' = H; n = 1)
B-3 (R = t-Bu, R' = Me; n = 0)

EXPERIMENTAL

General Details. Where necessary, experiments were conducted under nitrogen in a Vacuum Atmospheres drybox or using standard Schlenk techniques. Ether was sparged with nitrogen and passed through alumina columns. Butyllithium was used as received from Aldrich Chemical Company. 2-Bromobenzylalcohol, 2-bromophenol and *R*-fenchone were purchased from Aldrich and stored over 4 Å molecular sieves. 2-Bromo-6-t-butyl-4-methylphenol was prepared by known methods.[96] C_6D_6 and $CDCl_3$ were sparged with nitrogen and stored over 4 Å molecular sieves. ^1H and ^{13}C NMR data are listed in parts per million downfield from tetramethylsilane and were referenced using the residual protonated solvent peak. High resolution mass spectral analyses were performed at the MIT Dept. of Chemistry Instrumentation Facility.

2-Fencholphenol (B-1)

BuLi (35.60 mL, 2.60 M in hexanes, 92.48 mmol) was added dropwise to a -30 °C solution of *o*-bromophenol (8.00 g, 46.24 mmol) in ether (100 mL). After stirring for 2h, the reaction was recooled to -30 °C and fenchone (7.04 g, 46.24 mmol) was added. After stirring 12h, the reaction was quenched with NH_4Cl (aq). The layers were separated and the aqueous fraction was washed with ether (3 x 100 mL). The combined organic fractions were washed with $NaHCO_3$ (aq) and NaCl (aq), dried over $MgSO_4$, filtered and the solvent evaporated to give a yellow oil. The oil was dissolved in a minimal amount of MeOH and water was added dropwise until a cloudy white color persisted. The mixture was stirred at -30 °C overnight to give **B-1** as a white powder in two crops (6.71 g, 59.1 %). ^1H NMR (300 MHz, $CDCl_3$): 9.30 (s, 1, ArO*H*), 7.36 (d, 1, Ar*H*), 7.12 (t, 1, Ar*H*), 6.82 (d, 1, Ar*H*), 6.77 (t, 1, Ar*H*), 2.50 (br s, 1, O*H*), 2.33 (m, 2, fenchol), 2.12 (m, 1, fenchol), 1.81-1.72 (m, 2, fenchol), 1.54-1.41 (m, 1, fenchol), 1.38 (d, 1, fenchol), 1.32 (s, 3, fenchol), 1.25 (s, 3, fenchol), 0.57 (s, 3, fenchol). ^{13}C NMR (75.5 MHz, $CDCl_3$): 157.77, 128.57, 128.20, 127.68, 118.10, 117.72, 88.27, 53.32, 49.79, 45.75, 41.57, 33.51, 29.44, 24.47, 22.97, 17.86. HRMS Calcd for $C_{16}H_{22}O_2$: 246.161980; Found: 246.1622.

2-Fencholbenzyl Alcohol (B-2)

BuLi (32.92 mL, 2.60 M in hexanes, 85.60 mmol) was added dropwise to a -30 °C solution of 2-bromobenzyl alcohol (8.00 g, 42.80 mmol) in ether (100 mL). After stirring for 3h, the solution was recooled to -30 °C and fenchone (6.48 g, 42.80 mmol) was added. The reaction was stirred for 12h and then quenched with NH_4Cl (aq). The layers were separated and the aqueous fraction was extracted with ether (3 x 100 mL). The combined organic fractions were washed with $NaHCO_3$ (aq) and NaCl (aq), dried over $MgSO_4$, filtered and the solvent evaporated to give a white solid. Recrystallization from MeOH and water at -30 °C gave the product **B-2** as a white powder in two crops (6.35 g, 57.1 %). ^{1}H NMR (300 MHz, $CDCl_3$): 7.62 (d, 1, Ar*H*), 7.35 (d, 1, Ar*H*), 7.25-7.17 (m, 2, Ar*H*), 5.04 (d, 1 CH_2OH), 4.37 (d, 1, CH_2OH), 2.90 (br s, 2, O*H*), 2.45 (m, 1, fenchol) 2.08 (m, 1, fenchol), 1.83-1.73 (m, 2, fenchol), 1.56-1.41 (m, 1, fenchol), 1.40 (d, 1, fenchol), 1.33 (td, 1, fenchol), 1.23 (s, 3, fenchol), 1.21 (s, 3, fenchol), 0.49 (s, 3, fenchol). ^{13}C NMR (75.5 MHz, $CDCl_3$): 142.63, 140.67, 132.76, 129.57, 126.71, 126.23, 87.34, 67.10, 54.72, 50.05, 45.72, 41.57, 34.25, 30.37, 24.31, 23.33, 18.24. HRMS Calcd for $C_{17}H_{24}O_2$: 260.177630; Found: 260.1779.

2-t-Butyl-6-fenchol-4-methylphenol (B-3)

The same procedure was followed as for **B-1** and **B-2** on a 7g scale to give the product as white crystals (40.0% yield). ^{1}H NMR (300 MHz, C_6D_6): 9.72 (s, 1, ArO*H*), 7.12 (s, 1, Ar*H*), 7.07 (s, 1, Ar*H*), 2.24 (s, 3, ArCH_3), 1.88 (m, 1, fenchol), 1.67 (s, 9, C(CH_3)$_3$), 1.60 (m, 2, fenchol), 1.45 (s, 1, O*H*), 1.24 (m, 1, fenchol), 1.08 (d, 1, fenchol), 1.05 (s, 3, fenchol), 0.94 (m, 1, fenchol), 0.67 (s, 3, fenchol). ^{13}C NMR (75.5 MHz, $CDCl_3$): 155.02, 137.03, 127.73, 126.94, 126.07, 125.36, 88.35, 53.35, 50.05, 45.31, 41.42, 35.01, 33.64, 29.80, 29.25, 24.61, 23.16, 21.66, 18.14. HRMS Calcd for $C_{21}H_{32}O_2$: 316.240230; Found: 316.2409

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Curriculum Vitae

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Recitation Lecturer General Freshman Chemistry (5.11, 1997 and 1999)

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•Member MIT Women's Club Volleyball Team (2001)

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•Member of Junior Varsity volleyball team (1993-1996)

Acknowledgements

Running the New York City Marathon is a perfect metaphor for graduate school at MIT. It begins with a feeling of nervousness at the starting gun, a mixture of excitement and apprehension. Everyone else seems so confident and well-prepared, that it can seem intimidating at first. But as the crowd starts to run, you find your pace.

Right away, you are pushed to work your hardest because the first mile is straight uphill to the highest point of the race. At the top of this first hill, there is a view of Manhattan, where you will eventually finish the run. It is exciting to think about the finish already but it also reminds you that Central Park is very far away. So you turn your focus to running hard and working step-by-step.

As you run, sometimes you feel giddy with happiness at what you're accomplishing. Sometimes you feel overwhelmed with pain. Sometimes you feel like you're speeding along. Sometimes you feel like your progress is frustratingly slow. There are times when you walk to give your legs a break, because running harder and faster will only burn you out. There are times that are so smooth that you don't even think about your legs and the miles fly by.

You run through the five boroughs of New York City and, like the five years of grad school, each has a very different feel. Staten Island disappears in the blink of an eye. Brooklyn is exciting because you find your pace with fresh legs, but it also gives you the first taste of struggle with a few good hills. From Brooklyn, you cross into Queens and this is the halfway point of the run. By now, the pack of runners has spread out, and you often find yourself running alone. You cross a bridge into Manhattan and as you round the corner, you can hear the thousands of people waiting on the other side, cheering all the runners. You are literally blocks from the finish area in Central Park, but you still have 9 miles to run - it feels like you're so close, yet so far. The course takes you along 1st Avenue and into the Bronx, where all you think about is the finish line. Crossing back into Manhattan, you are on the last stretch! There is no turning back because you've come so far and you're almost there! You hustle through Harlem

and reach mile 22 - only four to go! But first, the roller coaster hills of Central Park - just when you think you must be closer to the finish, there's another hill to climb. Thankfully, for every challenging slope, there is an easy downhill and you keep your mind on the goal.

At mile 26, it's not quite over because a Marathon is 26.2 miles long. The finish line is right there, but it's at the top of one last hill. You find a last push of energetic spirit and you sprint to the finish. As you cross the line, smiling and arms stretched overhead, you experience a rush of feelings such as "I can't believe I just did that!" and "that was easy!". All of the hard work feels worth it and the struggles are quickly forgotten. You are given a medal and a water. The run is over.

The next day, the world around you hasn't changed and no one treats you any differently. You are still you. No one sees the medal that now hangs in your room, and all that's left are sore quadriceps for a few days. But you can feel it already, a sense of pride and wonderment about what you have accomplished and what you are capable of doing. This will be with you forever. If you can survive the Marathon, you can survive anything.

There is one constant source of motivation throughout the entire run and that is the people who cheer you on to finish, whether they be fellow runners or the spectators packed along the sidewalks. The encouragement from these people gives you inspiration to succeed and inspiration to cheer other runners onward. The best piece of Marathon survival advice I ever got was to write "Go Jenn" on my shirt so that there were always spectators or fellow runners there to cheer me on, yelling out my name, telling me I was so close, telling me to keep going, telling me that I had what it takes to make it to the end.

As with the Marathon, I reach the end of my Ph.D. having relied on the amazing support of my advisor, coworkers, friends and family. To all those who read this, know that your words of encouragement have carried me along through grad school. My experience has been remarkable thanks to you all!